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CONTENTS

Editorial

Hoover Urges Basic Research 185C

Technical Papers

Kinetics of Nickel-Sulfur and Steel-Sulfur Reactions. *Andrew Dravnieks* 435

The Oxidation of Iron-Nickel Alloys. *R. T. Foley, J. U. Druck, and R. E. Fryxell* 440

High Temperature Corrosion Rates of Several Metals with Nitric Oxide. *Milton Farber, Alfred J. Darnell, and Donald M. Ehrenberg* 446

Organic Peroxides as Source of Cations. *Andrew Gemant* 454

Electrodeposition of Molybdenum Alloys from Aqueous Solutions. *D. W. Ernst, R. F. Amlie, and M. L. Holt* 461

Periodic Current Reversal in Plating Copper-Lead Alloys. *Nelson W. Hovey, John L. Griffin, and Albertine Krohn* ... 470

Graphite Anodes in Brine Electrolysis, III. Effect of Anode and Operating Variables on Caustic Color. *M. Janes, N. J. Johnson, and E. B. Pilcher* 474

The Influence of a Surface Active Agent on the Electropolishing of Copper. *K. F. Lorking* 479

Mechanisms of Hydrogen Producing Reactions on Palladium. *James P. Hoare and Sigmund Schuldiner* 485

High Pressure Oxidation of Metals; Oxidation of Metals under Conditions of a Linear Temperature Increase. *John P. Baur, Donald W. Bridges, and W. Martin Fassell, Jr.* 490

Technical Review

Report of the Chlor-Alkali Committee of the Industrial Electrolytic Division for the Year 1954. *William C. Gardiner, Morton S. Kircher, and Warren D. Sherrow* 187C

Feature Section

Joy in Service (Presidential Address). *Marvin J. Udy* 188C

Current Affairs

Eppley Laboratory—ECS Sustaining Member 192C
Palladium Medal Award to U. R. Evans 193C
Further Details on Fall Meeting in Pittsburgh 194C
Cincinnati in Retrospect 195C

Highlights of the Meeting of the Board of Directors 196C
Section News 198C
Personals 200C
New Members 201C
ECS Membership Statistics 202C
Letters to the Editor 203C
Employment Situation 204C
Literature from Industry
New Products

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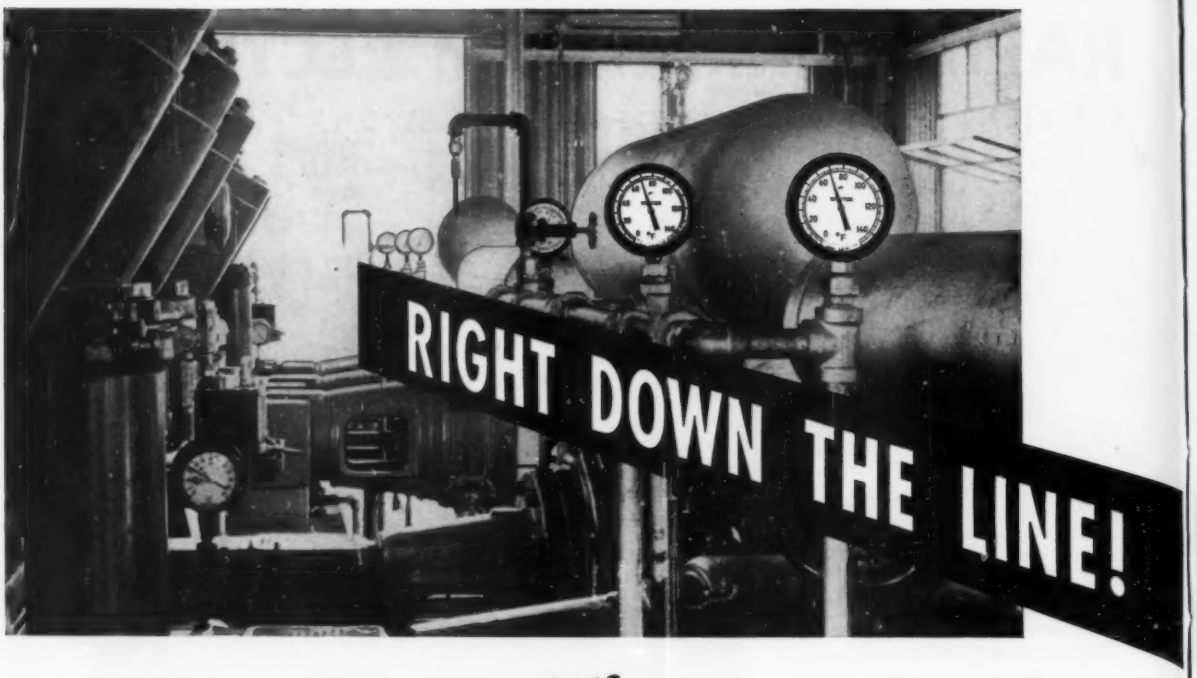

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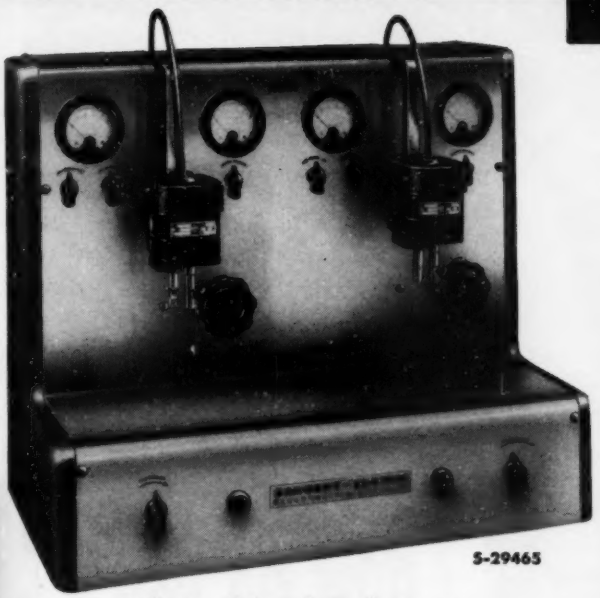

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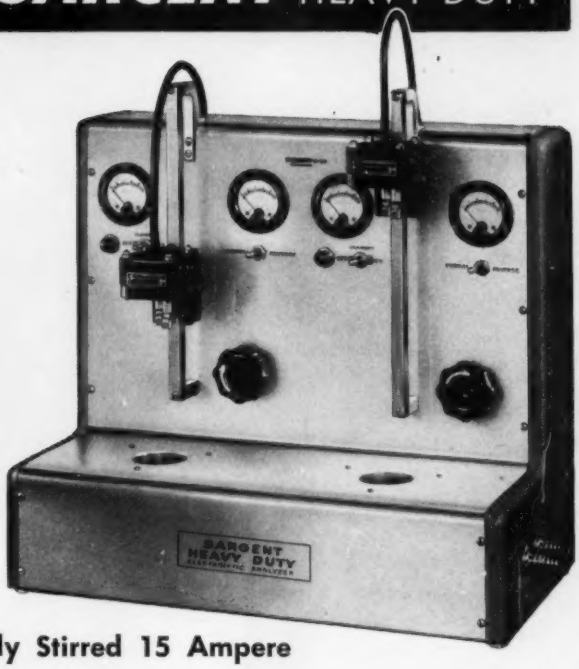

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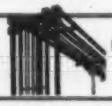

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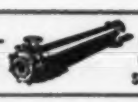

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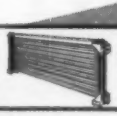

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Editorial

Hoover Urges Basic Research

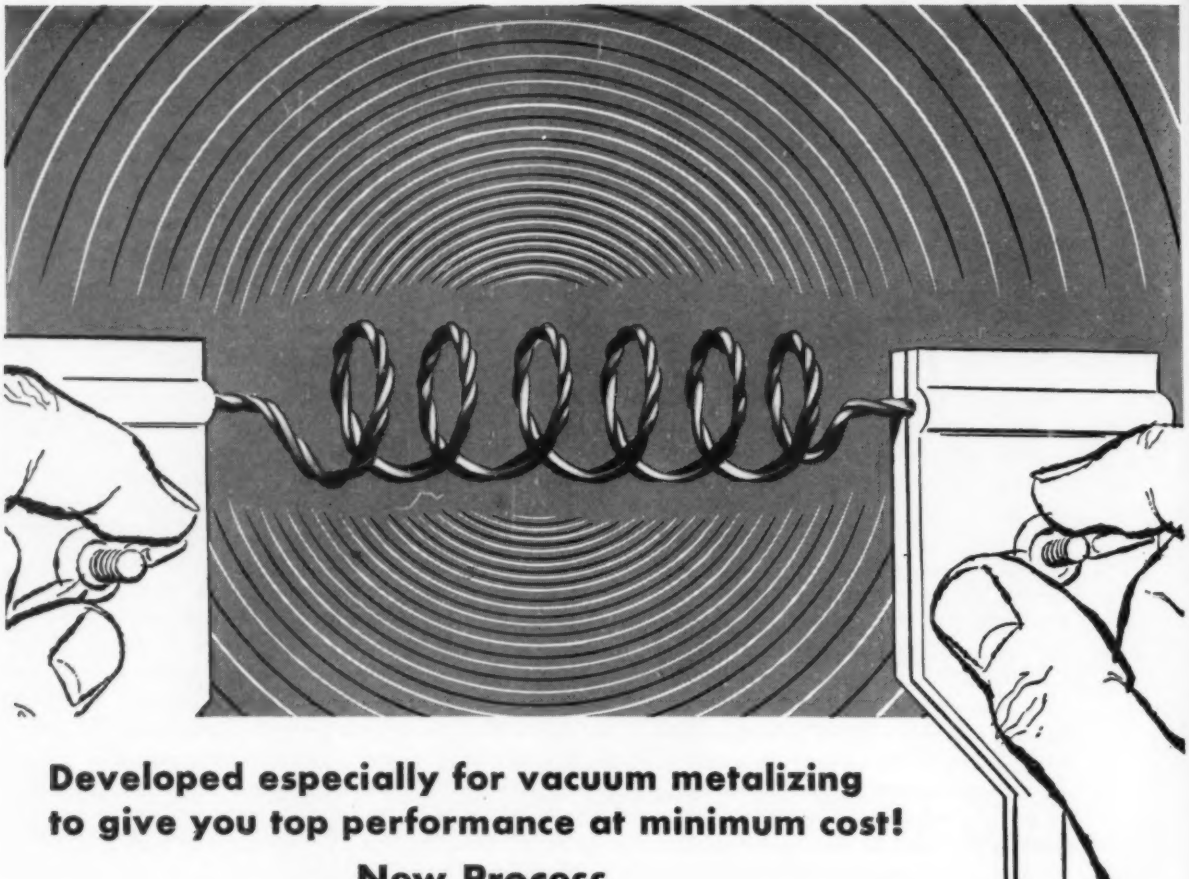
THE HOOVER COMMISSION is to be highly commended for its dramatic demand that the government give far greater support to basic research. In marked contrast to its previous recommendations for eliminating six billion dollars of federal spending, the Commission now urges that more money be spent for fundamental research in the physical sciences, biology, and medicine. It proposes a more clean-cut distinction between the effort in basic and applied science. There are many excellent suggestions for improving the administration of military research and these can be put into practice without Congressional action. The five general recommendations urging more federal support for basic research and the fifteen specific suggestions as to procedure were worked out by a task force of which M. J. Kelly, President of Bell Telephone Laboratories, was chairman. No more eloquent statement of the necessity for the augmented program can be formulated than appears in the preface of the Commission's report and is as follows: *The foundation of the greatest sector of human advancement in modern times is basic research into nature's laws and materials. It is from these sources that come the raw materials of applied science. We owe to basic research the fabulous improvement in the health of the nation; the greatest industrial productivity known to man; the weapons of defense which protect our independence; and our knowledge of the laws which govern the universe. There is no tribute great enough to express the nation's obligations to its scientists, engineers, and military personnel for their contributions to our constantly increasing productivity and the strengthening of our national defense. And there can be no relaxation in this effort.*

This report on the need for more basic research is a fitting climax in the activities of the Commission which went out of existence June 30. It will be recalled that this was the second Commission to be headed by former President Hoover. Its powers exceeded those of the first Hoover Commission in that it was authorized to suggest policy as well as procedural changes in government. The studies conducted by its thirteen task forces since the creation of the Commission in 1953 have pertained to budget and accounting, intelligence activities, lending agencies, medical services, overseas economic operations, paper-work management, personnel and civil service, procurement, real property, subsistence services, use and disposal of surplus property, water resources and power, and business organization of the Defense Department. It is to be hoped that its recommendations will fare as well as those of the first Hoover Commission, 72% of which have been put into effect.

"Electrochemistry in Biology and Medicine"

Under the above title the fifth volume in the Society's monograph series has appeared. This superb authoritative survey of current work and thought in the field has been edited and introduced by Dr. Theodore Shedlovsky of the Rockefeller Institute for Medical Research. He and the other eighteen scientists who have collaborated in the preparation of this excellent book have made a notable contribution to the application of modern physical science to biology and medicine.

—RMB



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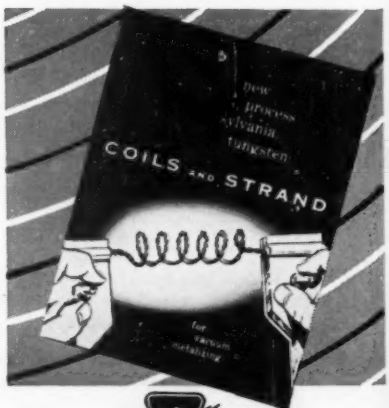

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Report of the Chlor-Alkali Committee of the Industrial Electrolytic Division for the Year 1954[1]

William C. Gardiner,[2] Morton S. Kircher,[3] and Warren D. Sherrow[4]

Production in 1954

The production of chlorine set a new record of 2,895,100 tons in 1954, an increase of 3.4% over 1953. Daily capacity is now estimated to be 10,600 tons so that the average production was 75% of the installed capacity. The year started with a low average of 7350 tons per day in January and gradually improved to 8400 tons per day which held for October, November, and December.

Caustic soda production was 3,393,900 tons, of which 14% was by the lime-soda process.

Changes in the Industry

The new plant of the Hooker Electrochemical Company at Montague, Mich., started in April and the chemical chlorine process plant of Hercules Powder at Brunswick, Ga., was started. International Minerals and Chemical Corporation expanded their caustic potash and chlorine facilities at Niagara Falls, N. Y. The Wichita, Kan., plant of Frontier Chemical Company expanded and a further expansion has been announced.

The Muscle Shoals caustic-soda chlorine plant was sold to Diamond Alkali in October and was expected to be in production early in 1955.

The Dominion Alkali Plant at Beauharnois, Quebec, has been sold to Columbia-Southern.

West Virginia Pulp and Paper Company shut down their plants at Covington, Va. and Tyrone, Pa., and are expanding their plant at Luke, Md., by replacing the Hargreaves-Bird cells with Hooker cells.

Dow Chemical Company built a plant to convert NaOH to Na_2CO_3 at Freeport, Texas.

General Aniline and Film Corporation announced their decision to build a 50 ton chlorine plant at Linden, N. J., using Mathieson cells.

Weyerhaeuser Timber Company has indicated that they will build a plant of 110 tons capacity at Longview, Wash. This will be the sixteenth paper mill with a captive chlorine plant.

Canadian Industries Limited announced that they would abandon their chlorine plant at Sandwich, Ont., which was partially destroyed when it sank into a brine well cavity. Expansion at Cornwall, Ont., will make up for the loss.

The price of mercury hurt mercury cell operators. Starting at \$187–\$189 per flask (\$2.46–\$2.49/lb), every price change was up until it reached an unprecedented \$325–\$330/flask (\$4.28–\$4.35/lb) in October. The year closed with the price at \$318–\$320 (\$4.19–\$4.21). In July the General Services Administration announced a three year guaranteed-price program which calls for buying a maximum of 125,000 flasks of domestic mercury and 75,000 flasks of Mexican metal at \$225 per flask. The program also provides for contracts with producers in other countries. Mercury cells use about 5% of the total U. S. consumption.

Oldbury Electrochemical Company started their sodium chlorate plant in Columbus, Miss.

Joshua Szechtman has announced his invention of a cell to produce metallic sodium, sodium-lead alloy, or caustic soda. It is still a paper development but is based on the old Acker process, also German work before and during World War II with the electrolysis of fused salt in a cell with a cathode of molten lead.[5] Szechtman's idea is to use a modern mercury cell design and substitute a thin stream of molten lead for mercury with fused salt as electrolyte. The sodium-lead alloy could be used directly for tetraethyl lead production. Sodium metal would be recovered by distillation or secondary electrolysis. Caustic soda would be made by blowing steam through the sodium-lead alloy.

Chlorine End Use

The end use pattern of chlorine for 1953 was published in *Chemical and Engineering News*, March 22, 1954, as follows:

Ethylene oxide and glycol	17.0
Pulp and paper	14.2
Carbon tetrachloride	6.8
Trichlorethylene	6.2
Tetraethyl lead fluid	5.6
Monochlorbenzene	5.0
Vinyl chloride	4.4
Direct treatment of water and sewage	4.0
Perchlorethylene	3.8
Propylene glycol	2.3
All other consumers	30.7
	100.0

During 1954 certain chlorinated solvents, plastics (vinyl chloride), and propellants (for aerosol bombs) made gains, while pesticides and herbicides (2-4D, 2-4-5T, etc.) and automotive fluids dropped slightly. Other uses remained about the same.

Literature

Three articles of interest to the chlor-alkali industry were published during 1954 in the JOURNAL OF THE ELECTROCHEMICAL SOCIETY:

"Diaphragm Type Amalgam Caustic-Chlorine Cell" by Chas. Potter and A. L. Bisio, p. 158.

"The *p*H in Chlorine-Caustic Electrolysis by the Mercury Cell Process" by Lars Barr, p. 497.

"Explosive Limits of Hydrogen-Chlorine Mixtures" by A. W. Umland, p. 626.

An excellent chapter on chlor-alkali technology was written by Dr. Karl Hass in Ullmanns "Encyklopädie der technischen Chemie," Urban and Schwarzenberg, München-Berlin (1954).

[1] Prepared for delivery before the Cincinnati Meeting, May 1 to 5, 1955.

[2] Olin Mathiesen Chemical Corporation, Niagara Falls, N. Y.

[3] Hooker Electrochemical Company, Niagara Falls, N. Y.

[4] Great Lakes Carbon Corporation, Niagara Falls, N. Y.

[5] Field Intelligence Agency Technical Report No. 830.

Feature Section

Joy in Service

Presidential Address*

Marvin J. Udy

Fellow members of The Electrochemical Society, distinguished guests, and friends:

You have done me a great honor in allowing me to serve as President of The Electrochemical Society. It has been an honor I never expected, and one that, I am sure, was not entirely deserved by the small service I have rendered the Society during my membership over the past 35 years.

It is a great honor that you do me tonight in listening to what is called "The Presidential Address." I assure you I will respect that honor and shall, in turn, honor you by being brief.

Your Society is now operating under the new Constitution and new Bylaws. It has been a long task to get them written and accepted. The Committee under whose direction these changes have been brought about is to be congratulated for the fine work they have done.

Your Society has had a good year, both financially and otherwise. Our finances are in good shape for the moment—thanks to our efficient Secretary, Dr. Henry B. Linford, and the efficient and loyal staff he has built up to handle the work of the National Office. Thanks also go to the wise handling of the Society's monies by Mr. E. G. Widell, who is now retiring after several years of service.

You will note that I have said "for the moment"; for many of us feel that we are operating in an era of good times. A reversal of this condition would quickly use up any reserves the Society has, and we would again be in trouble. However, the Ways and Means Committee has recommended to the Board specific means of building up our reserve, and I am happy to say the Board has adopted these recommendations.

There are other good reasons, I believe, that have contributed to the financial standing of your Society. These are, first, the excellence of the JOURNAL, and, second, the excellent programs put on by the Divisions of the Society. These two important functions of the Society have something in common that makes them so successful.

Let me discuss the JOURNAL first. It has attained the position of being one of the best, if not the best, in its field. The reason for this high position is due, I believe, to the continuity of our Publications Committee. Dr. R. M. Burns, as head of this Committee, with Dr. Norman Hackerman, Dr. Cecil V. King, and Mrs. Ruth Sterns have for a number of years constituted this Committee. They have not had to contend with an ever-changing Committee and, thereby, have been able to keep closely to the aims and high standards set for the JOURNAL. Their devotion to the JOURNAL has brought it to a position where it is now one of the best for recording new scientific work and improved processes in the principal fields of interest to the Society.

When it is realized that during the past year we had an income of about $20,850 from nonmember subscriptions, or about 70% of the dues collected by the Society, you can see how important the JOURNAL is to the well-being of the Society. In the past year nonmember subscriptions greatly helped to keep the Society operating in the black. I personally, and also for the Society, want to thank Dr. Burns, Dr. Hackerman, Dr. King, and Mrs. Sterns and her staff for the excellent work they have done.

Second, I would like to turn to the Divisions and those responsible for the programs at the conventions. As you know, each Division has a Chairman, Vice-Chairman, and a Secretary-Treasurer. It is the function of these chairmen to prepare programs for our conventions. Interest in the programs has been increasing steadily. At the Boston Meeting we had about as many nonmembers and guests as we had members; in fact, the rooms available would not accomodate the number of people who wanted to attend. The Boston Meeting was very successful from a scientific, technical, and financial standpoint. I want to thank the Boston Committee for the fine convention they put on.

There is a reason for these successful conventions, and I believe we will find it in the continuity of organization—just as in the Publications Committee. A Division Chairman and Vice-Chairman are elected for two years and, when the Chairman retires, the Vice-Chairman moves up; thus there is continuity of aims and purpose. When the ball is rolling it is easy to keep it rolling. The fine programs put on at the conventions have resulted in excellent material for the JOURNAL and help to maintain its high standards. These programs have resulted in several Monographs, which are also important as a means of recording work being accomplished in the scientific world, as well as a source of added income to the Divisions and the National Society.

Here, tonight, I wish to commend very highly and thank the Division Chairmen and Vice-Chairmen and their officers for the fine work they are doing. The work of these men is heavy and their time is given freely and enthusiastically. Without them we could not have such fine conventions.

Now, on the operation of your Society: your Society has become a rather big business. For the year ending January 1, 1955, some $83,800 worth of business was transacted.

I suppose every President of the Society experiences, in his year of office, certain problems that should be solved for the good of the Society, but about the time he has a partial grasp of the problems, his term is over. That is as it should be and I am not suggesting a longer term for the President as an answer to some of these problems. I do believe, however, closer cooperation of the Vice-Presidents with the President, and possibly two meetings of the President and Vice-Presidents each year should be mandatory. The purpose of these

* Delivered at the Cincinnati Meeting, May 3, 1955.

meetings would be to discuss the problems of the Society and agree on a continuity of program to be carried out for the good of the Society. In this way, continuity of the aims and purpose of the Society would be more uniform, and unity of purpose would result at the Board Meetings.

Furthermore, due to the different geographical locations of the Vice-Presidents, they might be given the additional duty of visiting the nearby Local Sections and, by so doing, much could be accomplished to create interest and activity in the Local Sections.

An $83,800 business has to be operated with continuity. True, if the President and three Vice-Presidents are working closely together with the aims and purpose of the Society agreed upon, it may not be so difficult. Trivial matters could be kept in their place and the Board's time spent on the more important and vital problems of the Society.

There is, I believe, something lacking in the functioning of the Board and I believe it is the lack of continuity. If the Divisions elect their officers to serve for two years, alternately, and operate so successfully, then why cannot the Board of Directors be elected in the same manner.

Likewise, there is nothing to provide continuity to the important Publications Committee, and it has kept its continuity simply because of the devotion of the members of this Committee and their willingness to serve under each new President and new Board of Directors, when the new President and new Board are willing to reappoint them.

It seems to me that, for a business of this size, the Board of Directors and Committees should be more permanent. Election for terms of two years, with a plan of alternate retirement and replacement, might work out to give more continuity to the Board. It is my hope that constitutional changes will be made in the near future to remedy these apparent weaknesses. The only other answer to this and other problems is a paid full-time business manager, full publicity, and intensified advertising through a proper medium. Your Society has grown up and is fast reaching a stage where it can no longer be run with an ever-changing Board of Directors and committees.

If we lived in the South and West we would hear more about "State's Rights." A fairly good-size dish of "States Rights" might help the Society. A revival of the Sections is needed and more work and more opportunities given them. True, we have created a new Advisory Council with two elected members from each Section, one elected each alternate year. The Advisory Council then elects two members to the Board of Directors. When properly operating, and fully participated in by the Sections, it should help give some continuity to the Board and also give the Sections a more direct part in National Society affairs. This is not enough, and more should be done to increase the activity in the local sections. The National Society is no stronger than the Sections and the Divisions. Incentive should be given to revive and increase activity in the Sections.

How this revival of the Sections is needed is shown by the following data. As of May 1st we have:

Active Members	1975 including Life Members
Honorary Members	5
Sustaining Members	103
Emeritus Members	37
Associate Members	60
Student Members	41
Total	2221

Breaking this down by Sections the situation is as follows:

Chicago	107 members
Cleveland	165
Detroit	75
India	24
Midland	37
New York	415
Niagara Falls	126
Pacific Northwest	36
Philadelphia	160
Pittsburgh	79
San Francisco	40
Washington-Baltimore	109
Ontario-Quebec	53
	1426
Non-Section	795
Total	2221

New Members added to April 13, 1955:

Active New Members	182
Estimated resignations and deaths	70
Net Gain	112

This is a gain of 5% and is not enough to keep the Society in a good, healthy condition.

For the good of the Society we need new members; we need young men who are willing to serve. To the young man who is asked to become a member of the Society and replies. "What do I get out of it," the answer is, "What can you give the Society; what service can you render?" I might answer the question by stating what the Society has given me for the little service I have rendered. The Society has given me, first, a chance to associate with the leaders of the industry from which I have made my living; second, a place for publication of my work whenever it meets the high standards set up by the Society; third, a chance to take part in local sections and to associate with local leaders; fourth, a chance to attend national conventions and to see and hear what others are doing in my particular field and other related fields; fifth, a chance to be of service to others. All this helps in the growth and development of the individual to something above the average. Think of the men I have known in The Electrochemical Society! Here are the names of some of them: Wilder D. Bancroft, F. J. Tone, Walter S. Landis, A. T. Hinckley, H. C. Parmelee, F. M. Becket, William Blum, S. C. Lind, Paul J. Kruesi, Francis C. Frary, Louis Kahlenberg, Bradley Stoughton, Hiram S. Lukens, James H. Critchett, Duncan MacInnes, William G. Harvey, Robert L. Baldwin, H. Jermain Creighton, F. C. Mathers, R. R. Ridgway, Edwin M. Baker, R. M. Burns, S. D. Kirkpatrick, W. C. Moore, George W. Heise, J. A. Lee, A. L. Ferguson, Charles L. Faust, Ralph M. Hunter, J. C. Warner, R. J. McKay, and a host of members, prominent in scholastic work and in industry. Each and every one has had some influence on my life and has made it better. What more does the young man want?

The Electrothermics and Metallurgy Division has made a long step in the direction of interesting young men in electrothermics and metallurgy. In the past year, through the efforts of their efficient Chairman, Dr. I. E. Campbell, and Vice-Chairman, Arthur Haskell, and the Executive Committee, they have evolved a plan of giving awards to students interested in the field. The funds for these awards are to be sup-

plied by industrial companies, and the award is to be named after some prominent man in the company contributing to the award. I am happy to announce that our first award will be the Dr. F. M. Becket award. Dr. Becket was an active member of the Society and a Past President. He was founder of The Electrometallurgical Company, a Division of the Union Carbide and Carbon Corporation. The Electrometallurgical Company is graciously contributing the sum of $10,000, the income from which is to be used for a limited scholarship to a deserving freshman or a senior interested in the field of electrothermics and metallurgy. The Society is grateful to The Electrometallurgical Company, and they have our sincere thanks for their support.

Further activity must come from the Sections and Divisions. I believe the Becket award has opened the way for many more such scholarships.

Finally, we hear much in these days of the need for scientists and science teachers. Our JOURNAL, as well as many other like journals, has been publicizing this need. True, we need scientists and science teachers, but we also need men; we need men steeped in the tradition of our forefathers, men of character, men who know their proper relation to their fellowmen, men with dignity, well balanced men, and self-reliant men. In this day and age of atomic science, when the central government has grown to an all powerful state, we need men and women of faith, vision, courage, who are unafraid to shoulder the responsibilities of freedom, and willing to take back our rights to the state, to the county, to the city and to every hamlet, that we might take care of our own with the least interference from the national government. Yes, we need men and women who know from whence they came, why they are here, and whither they are going—who are willing to shoulder the burdens of freedom lest we lose our freedom. Without freedom there would be no need for scientists and science teachers.

Again, let me thank you for the privilege of serving you to the best of my ability. I assure you, whatever service I have rendered to the Society, no matter how small, has been a great pleasure to me and Mrs. Udy, and I wish for all of you the best of everything.

MANUSCRIPTS AND ABSTRACTS FOR SPRING MEETING

Papers are now being solicited for the Spring Meeting of the Society, to be held at the Mark-Hopkins Hotel in San Francisco, April 29 and 30, and May 1, 2, and 3, 1956. Subjects to be covered at the technical sessions will be Electric Insulation, Electronics (including Luminescence, Oxide-Cathodes, Phosphor Application, Semiconductors, and Instrumentation), and Industrial Electrolytics, and probably Electrothermics and Metallurgy and Theoretical Electrochemistry.

To be considered for this meeting, triplicate copies of abstracts (not to exceed 75 words in length) must be received at Society headquarters, 216 West 102nd St., New York 25, N. Y., *not later than January 2, 1956.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

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The Fall 1956 Meeting will be held in Cleveland, Ohio, October 28, 29, 30, and 31, and November 1, at the Statler Hotel. Sessions will be announced in a later issue.

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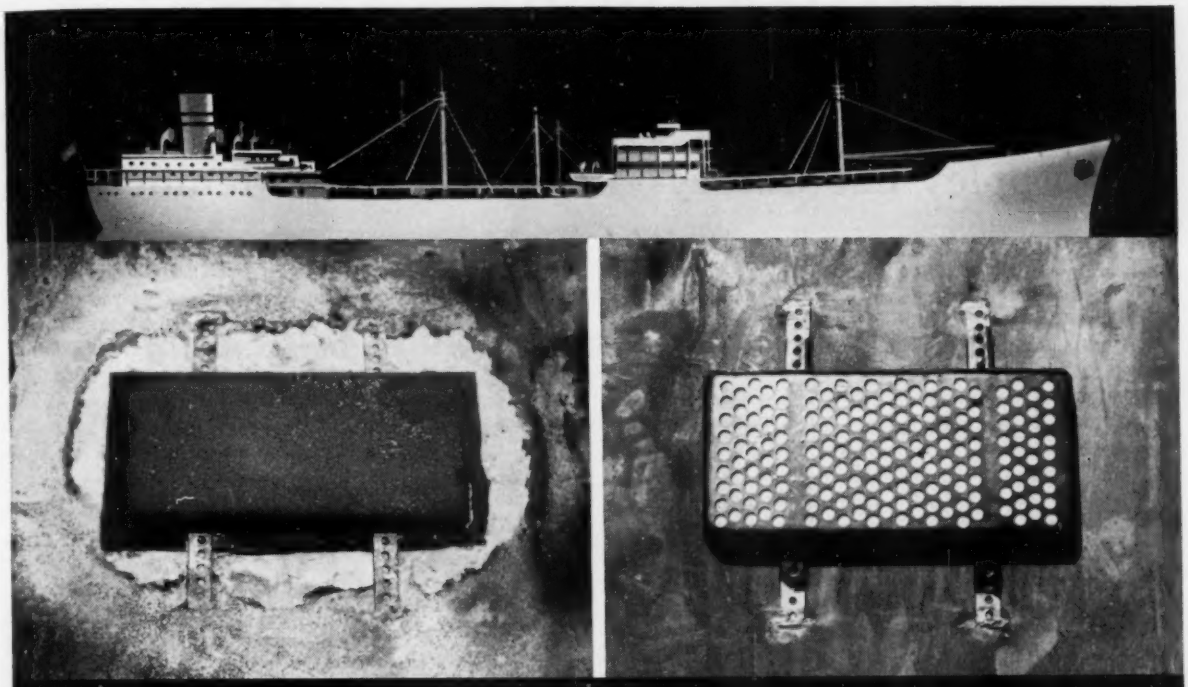

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Current Affairs

Eppley Laboratory—ECS Sustaining Member

The founding of the Eppley Laboratory as a producer of standard cells for industrial and laboratory purposes came about nearly 40 years ago through a fortuitous combination of circumstances.

In 1915, when the tempo of the First World War was rapidly increasing in Europe, Marion Eppley was a graduate student at Princeton, working for his Ph.D. degree. One day, having entertained at luncheon a representative of Leeds & Northrup Company of Philadelphia, he took his guest on a tour through the first Eppley Laboratory—a compact but complete basement and attic laboratory in which he was engaged in research work in electrochemistry connected with his doctor's thesis. The guest's marked interest, upon being shown some of Eppley's "home-made" standard cells, was not difficult to understand when he explained that the war had cut off the supply of standard cells from Europe, and that the manufacture of a line of potentiometric instruments for temperature determinations depended upon locating a domestic source of these cells having certain technical characteristics. Arrangements were quickly made for Eppley to supply Leeds with an initial order of 25 units, and the young industry was on its way.

Before long it became obvious that the United States would soon become involved in the spreading conflict, and Eppley enrolled in the United States Naval Reserve with the rank of Lieutenant-Commander of the line. Ordered to Newport, R.I., as Ordnance officer of the Second Naval District, he was faced with the problem of fulfilling his military duties and at the same time continuing the manufacture of standard cells, now a function of constantly increasing importance.

The problem was solved by the loan—a permanent loan, as it turned out to be—of the services of William R. Gray, a young electrical engineer in the employ of Leeds & Northrup. Gray went to Newport, where he was installed in a cottage—still an integral part of the Eppley Laboratory—in the basement of which he proceeded to build standard cells, tutored by Lieutenant Commander Eppley during the latter's "spare" time. (This was at night after the hours of naval duty. Work on cells often ran until two or three o'clock in the morning.)

In the years following the armistice the plant expanded as the production of cells increased. The public was eager for the consumer goods denied it during the conflict, and the demand for more accurate, automatic controls of industrial processes became greater as industry sought to supply the public's needs.

A program of constant improvement and development of standard cells was always foremost, even in the earliest days. With a small though enlarged staff under the direction of Dr. Eppley, now freed from his naval duties, methods of preparation of materials were developed, and analytical checks on purity instituted. Many of these are still in use today.

Cadmium and cadmium sulfate are purchased in the purest forms commercially obtainable. The metal is further purified by distillation, and each lot analyzed spectroscopically before use. The salt, each lot of which is similarly analyzed by an independent laboratory as well as by the Eppley staff before purchase, is dissolved in distilled water, recrystallized, and analyzed again before being made into the final cell solution. Mercury is cleaned by oxidation, washed, redistilled, and checked against standards of exceptional purity.

In addition to the large-scale production of unsaturated cells—the "pyrometer type" for use in industrial processes and the "precision type" for research and laboratory work—the firm has paid particular attention to the construction of saturated cells for customers who wish to establish banks of standards comparable to those of the National Bureau of Standards in Washington. Among the foreign governments purchasing these standards have been those of Israel, New Zealand, China (in the 1930's), and the Union of South Africa. Precision saturated cells, since they cannot be shipped, must be carried by messenger, and in several instances physicists from these distant nations have come to the United States to visit at the National Bureau of Standards and elsewhere, picking up their cells in Newport.

During the period between the two World Wars other products were developed: a line of precision d-c measuring instruments, thermopiles of various types, and the Eppley pyrheliometer for the measurement of total solar and sky radiation. The latter instrument, a form of the Weather Bureau type described by Kimball and Hobbs, has been adopted by the U.S. Weather Bureau. It, too, has penetrated to far parts of the globe, units having found their ways to Portugal, Finland, Hawaii, the Belgian Congo, Macao, Israel, Angola, and many other places.

With the advent of the second great war, Dr. Eppley returned to active Naval Reserve duty in the rank of Captain. At the laboratory, the production of standard cells rose to an all-time high, taxing the facilities of the small plant to the utmost. There was also considerable activity on classified Government contracts, largely in the field of radiation.

Interest in thermal detectors has increased in the years following the cessation of hostilities. One new product is the Golay Pneumatic Infra Red detector. This unique detector, now widely used in infrared spectroscopy, has an exceptionally high sensitivity and a remarkably short time constant. A further application for it has recently been found as a detector in the millimeter wave region.

Research on standard cells has also continued, the main object being the elimination of temperature hysteresis. One phase of this work was climaxed in 1951 with the presentation at the Symposium on Electrochemical Constants, held at the National Bureau of Standards in Washington, of a paper[1] on standard cell septa by Dr. Eppley and George D. Vincent of the Laboratory staff. It was conclusively shown that the impurities which leached out from untreated or improperly treated cork septa were responsible to a large degree

[1] M. Eppley and G. D. Vincent, "Septa in Standard Cells," NBS Circular 524, August 1953.

for the perhaps unimportant but determinable erratic behavior of portable unsaturated cells during a rapid cooling following an elevation of ambient temperature.

Concurrent with this research ran the development of plastic septa. All Eppley "miniature" cells are provided with the patented septa resulting from this work, and it is anticipated that similar septa will soon be employed in other types of cells as well.

Plans for the present and future direction of research include the further development of miniature cells and the production of a cell capable of withstanding greater current drains than standard cells have been subjected to in the past. The latter aim conflicts with the principle of "miniaturization," as it appears that "current drain" cells will have to be larger rather than smaller, but it is confidently expected that this problem will be solved.

Palladium Medal Award to U. R. Evans

Ulick Richardson Evans of Cambridge, England, has been selected by The Electrochemical Society as 1955 Palladium Medalist. Dr. Evans will receive the third impression of the medal at the banquet on October 11, held in connection with the Fall Meeting of the Society at Pittsburgh, Pa.

Dr. Evans is a distinguished scientist, who has written five books and about two hundred papers on electrochemistry and corrosion. He has probably done more than any other individual to place the corrosion of metals on a quantitative, scientific basis. On the fundamentals elucidated by Dr. Evans is based most of the engineering progress that has advanced the prevention of corrosion to such a high stage of development during recent years.

His first book, "Metals and Metallic Compounds," was published in four volumes in 1923. During the writing of this book he became impressed by the lack of scientific knowledge of corrosion processes. Thus he started the work on this subject for which he became famous. In 1924 his book on "The Corrosion of Metals" was published. This was subsequently translated into German, French, and Russian, and was followed by a second edition in 1926.

In 1937 his book "Metallic Corrosion Passivity and Protection" was issued. This was probably the most comprehensive book ever written by one man on corrosion and protection.

His latest book, "An Introduction to Metallic Corrosion," was published in 1948.

The top floor of the old Chemical Laboratory Building, Pembroke Street, in Cambridge was the scene of most of Evans' experimental work. He excelled in designing and carrying out critical experiments with a minimum of complicated equipment. His interest in the theory of probability and applications

U. R. Evans

of statistics began at an early age, and he was quick to apply these valuable tools to the study of corrosion.

His fame in his chosen field attracted numerous research students to him. Men from many foreign countries, as well as from the British Isles, worked in his laboratories under his guidance. It was a stimulating and valuable experience for all of them.

Honors also came to him as a result of his work. He was awarded a D.Sc. degree from Cambridge University in 1932 and from Dublin University in 1947. He received the Armourers' and Brasiers' Research Fellowship from the Royal Society in 1933, and the Willis Rodney Whitney Award of the National Association of Corrosion Engineers in 1948. He was elected Fellow of the Royal Society in 1950.

Dr. Evans retired from his formal connection with Cambridge University in the fall of 1954 but he remains active in carrying out research in corrosion and as chairman and member of various committees in this field.

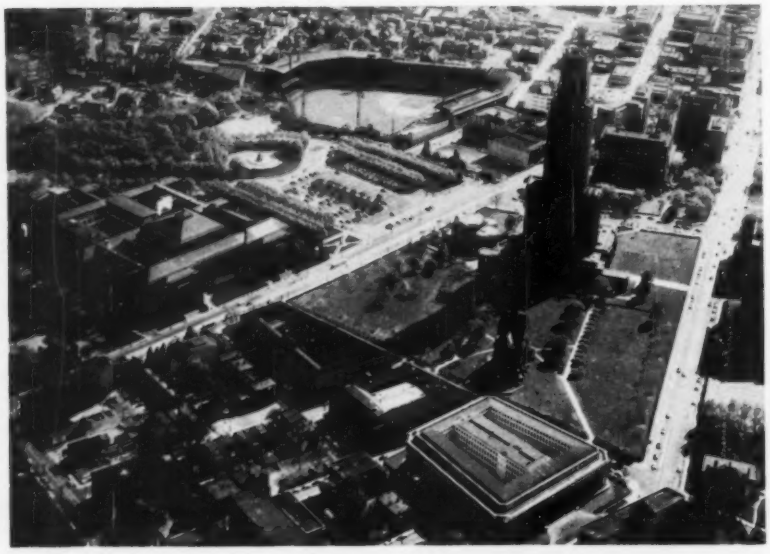
The first Palladium Medal Award was conferred on Dr. Carl Wagner in 1951, then Visiting Professor of Metallurgy at Massachusetts Institute of Technology, during the Fall Meeting of the Society in Detroit. The second Palladium Medal was awarded to Dr. Nathaniel Howell Furman, of Princeton University, in 1953 during the Society's Fall Meeting in Wrightsville Beach, N. C.

The metal used for the medal, and its design, have an interesting significance in connection with the award. The use of palladium explains the selection of the figure of the Greek goddess, Pallas Athene, which appears on the back of the medal, and after whom palladium, a member of the platinum group of metals, was named. Alchemical symbols of other metals surround the figure of the goddess, who, according to mythology, protects materials against destruction by the elements. Thus, the metals are secure against the corrosive influence of their environments.

Pittsburgh Program Booklet Not to be Mailed Separately

For the Pittsburgh Meeting, separate Program Booklets *will not* be mailed to members of the Society. For this meeting complete information, which in the past has appeared only in the Program Booklet, will be included in the September issue of the JOURNAL. In other words, the September JOURNAL will carry General Information, Technical Program, and Abstracts. Reprints from the JOURNAL will be available at the Pittsburgh Meeting in the former Program Booklet size.

Further Details on Fall Meeting in Pittsburgh



Pittsburgh's Oakland Civic Center, showing Carnegie Institute, Mellon Institute, University of Pittsburgh.

Members of The Electrochemical Society will get first-hand information about the current Pittsburgh renaissance when they attend the Fall Meeting of the Society. Those who have known this mighty Pennsylvania city in the past need only to look around and watch the old landmarks crumbling. And in their places they will see the first evidence of a planned expansion and modernization—big buildings of stainless steel and aluminum; huge bridges and long tunnels to provide straight and speedy traffic arteries over undulating topography; plus new centers of culture and engineering to spark a continuing development that promises to make Pittsburgh one of America's leading cities.

Thus the empirical facts of Pittsburgh's redevelopment can be ascertained by direct observation and by a study of plans fresh off the drawing board. But what about the mechanism of this transformation? By what paths does a city undergo such changes? What interaction between government and industry is necessary, and what "activation energy" is required to carry out the process at a reasonable rate? The answers to such questions will be presented at a Society Luncheon on Monday, October 10, by a man who has had a prominent part in Pittsburgh's redevelopment—the Hon. John P. Robin, Secretary of Commerce, Commonwealth of Pennsylvania.

According to Paul Fugassi, General Chairman of the fall convention, practical information on what to do and where to eat in Pittsburgh will be disseminated to the Society members and their wives during a get-acquainted-hour planned for Monday afternoon. Plant trips to representative industries in the Pittsburgh area are also planned —a steel plant, a power station, a chemical plant, and last, but perhaps not least, a brewing company or two.

The city of Pittsburgh also holds considerable interest for the ladies, according to Mrs. R. A. Woofter, Chairman of the Ladies' Committee. A sight-seeing tour of Fort Ligonier, part of the Pennsylvania Turnpike, and the scenic countryside near Pittsburgh have been arranged for them. In addition, they will be conducted through the new aluminum building of Alcoa and the H. J. Heinz Co. plant (the latter company is in the food business).

On the strictly social side, a theater party will be held at the Pittsburgh Playhouse on Wednesday evening, October 12.

Complete details on the meeting, including the technical program, will appear in the September JOURNAL.

Employment Posters for Pittsburgh Meeting

Companies which desire to recruit employees at the Pittsburgh Meeting, October 9 to 13, 1955, are invited to prepare posters (not to exceed 8½ in. × 11 in.) to be placed on a bulletin board near the registration desk.

Company representatives can contact Mr. Robert A. Woofter, Registration Chairman, during the meeting to make arrangements for posters to be displayed.

Battery Round Table on "Aging" Problems in Batteries

The Battery Division is planning an all-day Round-Table Discussion at the Pittsburgh Meeting. The date has been set tentatively for Tuesday, October 11. The session will cover processes which limit the shelf or storage life and the charge retention of batteries.

The ideal battery, completely inert except when electrical energy is being withdrawn or stored, does not exist. Primary cells age by loss of water or electrolyte, by corrosion of anodes, and by degeneration of separators and cathode materials. Storage batteries lose charge while standing on open circuit, lead-alloy grids corrode, separators degenerate, and irreversible changes may take place in the active material of either plate.

These side reactions present limitations to users of batteries, and a challenge to their manufacturers. An informal discussion of the symptoms, the causes, and the cures for these diseases should interest all members of the Battery Division. The present plans call for a brief introduction to each subject by one of a panel of speakers, to be followed by general discussion from the floor.

More complete details of the program will be sent to each member of the Battery Division. Nonmembers of the Division can be added to the mailing list for this program by sending their names and addresses to Mr. E. J. Ritchie, Eagle-Picher Co., Joplin, Mo.

Cincinnati in Retrospect

Snapped at the Cincinnati Meeting. I—F. A. Lowenheim, L. I. Gilbertson, M. J. Udy, and R. O. McDuffie (General Chairman of the Meeting); II—W. C. Moore, A. T. Hinckley, and Sherlock Swann, Jr.; III—N. M. Winslow and G. W. Heise; IV—Leila Hollander, C. V. King, and H. T. Francis; V—Norman Hackerman and Mrs. Quentin McKenna; VI—Mrs. Udy, M. J. Udy, Julian Glasser, R. A. Woofter, and Mrs. Woofter; VII—A. C. Loonam, W. C. Gardiner, A. C. Haskell, Jr., and K. E. Kundel; VIII—A. L. Ferguson, F. C. Mathers, and A. T. Hinckley; IX—H. B. Linford, Julian Glasser, and Mrs. Linford; X—E. G. Widell, H. R. Neumark, and H. C. Miller. (Photographs by Ben Rosen, Cincinnati)

Semiannual meetings of the Society grow bigger, and, it is hoped, better each year. The Cincinnati Meeting, May 1 to 5, 1955, broke all records. Let's take a look at the record.

Meeting	Date	Attendance, including ladies and guests
Washington	April 8–12, 1951	595
Detroit	Oct. 9–12, 1951	434
Philadelphia	May 4–8, 1952	672
Montreal	Oct. 26–30, 1952	417
New York	April 12–16, 1953	696
Wrightsville Beach	Sept. 13–16, 1953	364
Chicago	May 2–6, 1954	733
Boston	Oct. 3–7, 1954	562
Cincinnati	May 1–5, 1955	925

Cincinnati outdistanced all of its predecessors on number of registrants and number of technical papers scheduled. To become bigger is not enough; the Cincinnati program also had quality of papers and variety.

Monday morning at the Sheraton-Gibson Hotel there were so many people to be registered for technical sessions that things got a bit stacked up and confused, but members and guests, with their usual good humor, queued up and got acquainted. As registration climbed, shortages of supplies developed but, these, too, worked themselves out. Meeting room assignments were shuffled around, but, as far as we know, everyone got located satisfactorily.

Monday evening's informal buffet supper was highly successful from the diner's point of view and well attended

from the local committee's point of view. The planned entertainment broke up early enough to permit out-of-towners to investigate Cincinnati and its environs. Both were interesting and instructive.

The Annual Business Meeting and luncheon on Tuesday had an unusually large attendance; word of Dr. Gustav Eckstein's prowess as a speaker must have made the rounds in advance. As he talked one could see members observing each other, nonsmokers watching smokers light up with interest and, perhaps, envious understanding. Dr. Eckstein discussed the psychology of hands, what people did with them as they talked, what painters did with hands in art to produce certain results and emotion; he made the simple (!) act of lighting a cigarette a highly complex and rather involved procedure. Check the motions through which you go to get a drag; you'll see how busy it keeps your hands.

On Tuesday evening, when President Udy completed his address members and guests rose to their feet clapping. You can read his talk on page 188C of this issue and those who didn't hear him can get, thereby, an inkling of the reason for the ovation. President Udy was brief, spoke sincerely, and on a subject close to those who attend meetings, the Society itself.

The Local Committee which organized and ran the meeting earned a vote of thanks from the Society. There is no Local Section in the area so credit goes to R. O. McDuffie and his committeemen for the fine job they did in handling the Society's largest meeting.

Highlights of the Meeting of the Board of Directors

(Held May 1, 1955, Hotel Sheraton-Gibson, Cincinnati, Ohio)

President M. J. Udy announced that he had just received a communication from Mr. A. L. Foscue, President of The Electrometallurgical Company, indicating that Electromet would turn over to The Electrochemical Society $10,000 for an F. M. Becket Memorial Award. Messrs. Ivor Campbell, A. C. Haskell, G. M. Butler, A. T. Hinckley, M. J. Udy, and J. H. Brennan were appointed as a committee to recommend details for the award.

On motion of Dr. H. H. Uhlig, it was voted that the Board express its appreciation for the services rendered the Board by Mr. E. G. Widell these past years. The yearly report of the Treasurer has been published in the July JOURNAL.

On motion of Dr. L. I. Gilbertson, it was voted that the Report of the Auditor be accepted. The audit has been published in the July issue of the JOURNAL.

The Secretary then requested a change in the budget for the coming year. Due to the cash system of bookkeeping, the probability of an error having been made on estimated income from nonmember JOURNAL subscriptions was so high that the Secretary requested reducing the budgeted income from this source from $25,000 to $22,000 and at the same time to reduce the budget for printing and mailing of the JOURNAL from $31,000 to $29,000. This would still leave the budget in the black. On motion of Dr. F. A. Lowenheim, it was voted that the proposed budget changes be made.

Due to incomplete returns from a mail canvass of the Board, the matter of a reader's service card was discussed at some length, the final decision being to try this for a three-month period.

The Chicago Convention financial statement was presented and approved.

The Ways and Means Committee recommended that the Secretary arrange for an insurance policy to take care of sick leave on the basis that the Society pay ⅔ of the premiums and the employees ⅓. On motion of Mr. R. J. McKay, it was voted that this recommendation be accepted by the Board.

At the recommendation of the Ways and Means Committee, and on motion of Dr. Uhlig, it was voted that the accepted retirement age of office employees be 65 years. However, any case may be reviewed by the Board.

The Ways and Means Committee then recommended the setting up of a General Society Reserve Fund, and that monies for this purpose be obtained from two sources. First, increase the nonmember JOURNAL subscription rate from $15 to $18, and increase the differential between member and nonmember registration at meetings by $3 (this would mean that if a member's registration costs $7, nonmember registration would be $13). The additional money obtained from these two sources would be put into the General Society Reserve Fund. On motion of Mr. McKay, it was voted to accept this recommendation.

On motion of Mr. McKay, it was voted that the program booklet publication be made by printing the program in the JOURNAL and preparing the reprints for distribution at the meetings.

On motion of Mr. McKay, it was voted that nonmember invited speakers may register at national meetings at the expense of the national Society, provided that the Division chairman involved so recommends to the Society. It was agreed that the Secretary would mail to the invited individual a card for presentation at the time of registration, stating this fact.

The Ways and Means Committee presented the following tentative schedule for meetings:

Spring 1959—Philadelphia
Spring 1960—Chicago
Spring 1961—Knoxville
Spring 1962—Boston
Spring 1963—St. Louis
Spring 1964—Washington
Fall 1959—Columbus
Fall 1960—Houston
Fall 1961—Detroit
Fall 1962—Pacific N. W.
Fall 1963—New York
Fall 1964—Toronto

On motion of Mr. McKay, it was voted that the Secretary arrange with the chairmen of the various local sections for a speaking tour of the President to include those sections that desire such a session, and that the financial arrangements be made by the national office, but that payments go directly from the Section to the President after all commitments have been made.

The Electrothermics and Metallurgy Division asked for a decision from the Board regarding their volume "Vacuum Metallurgy." Since John Wiley did not desire to print this, due to their market survey indicating insufficient sale, the Division proceeded with publication. They plan to sell the volume at $5 for nonmembers and $4 for members. The bill for the publication would be approximately $950. Dr. I. E. Campbell presented two plans: one for the Society to include it with its regular monograph series, under which circumstances, after costs the profits would be split 60-40 between the Society and the Division; under the second plan the Division

would underwrite the entire operation, retaining all profits. On motion of Dr. Campbell, it was voted that the Society underwrite the operation and that this volume be considered one of the monograph series.

The Secretary announced that the Young Author's Prize winner was M. J. Pryor for his paper "The Protective Action of Pigments on Steel," and the Francis Mills Turner Memorial Award, Sponsored by the Reinhold Publishing Corporation, winner was D. A. Vermilyea for his paper "Formation of Anodic Oxide Films on Cathodes."

President Udy then turned the meeting over to Dr. Uhlig for committee appointments. Dr. Uhlig appointed Dr. John Musgrave as Chairman of the Membership Committee and Dr. Ralph Hunter as Chairman of the Nominating Committee, the latter committee being composed of I. E. Campbell, E. B. Yeager, C. L. Faust, and Paul Delahay. These appointments were approved.

The Secretary then resigned, at which time the Board voted to reappoint him for the succeeding year.

The meeting adjourned at 5:30 P.M.

HENRY B. LINFORD, *Secretary*

Highlights of the Meeting of the Board of Directors

(Held May 3, 1955, Hotel Sheraton-Gibson, Cincinnati, Ohio)

The President reported that Mr. G. W. Heise had expressed a preference to include his gift of approximately $1000 (*See* Board minutes published in the December 1954 issue of the JOURNAL) in Union Carbide and Carbon common stock in the General Society Reserve Fund. On motion of Dr. H. H. Uhlig, it was voted to include this principal sum in our General Society Reserve Fund.

The following committee appointments were made by the incoming President, H. H. Uhlig:

Ways and Means Committee

F. A. Lowenheim, *Chairman*
R. M. Hunter
R. A. Schaefer
G. W. Heise
M. J. Udy
S. Swann, Jr.
E. B. Yeager

Finance Committee

L. I. Gilbertson, *Chairman*
F. A. Lowenheim
H. B. Linford
E. G. Widell
Hans Thurnauer

Patent Committee

This was referred to the Ways and Means Committee.

Publicity Committee

This was referred to the Ways and Means Committee.

Sustaining Membership Committee

This committee is being worked on.

Admissions Committee

Louis Weisberg, *Chairman*
L. I. Gilbertson
H. Bandes

Publication Committee

R. M. Burns, *Chairman*

The Secretary requested approval of the Bylaws of the Electrothermics and Metallurgy Division. These bylaws had been distributed several months before. On motion of Dr. Uhlig, it was voted that the bylaws, as distributed, be approved.

The Secretary then reported that the Publication Committee had requested restoration of the $2000 in the budget for the printing and mailing of the JOURNAL that had been removed at the May 1 Board Meeting. It was further noted by the Secretary that this deficit now most likely will be met by the Cincinnati Convention, and since the Society is underwriting the Pittsburgh Meeting, also, the budgeted amount of net income from meetings could be raised by this $2000, retaining the budget in balance. Therefore, on motion of Dr. Norman Hackerman, these budgetary changes were made.

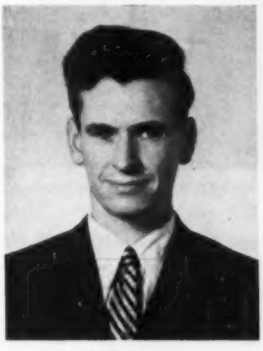
Dr. R. M. Hunter reported for the Ways and Means Committee that they would like to have a Survey Committee appointed to study the present affairs and the future outlook for the Society. On motion of Dr. Uhlig, it was voted that the Board would approve such an appointment; Dr. Ralph Schaefer is to be Chairman. This committee would report to the Board through the Ways and Means Committee.

The situation with respect to Mr. William J. Holian, Assistant Secretary, was reviewed. Due to Mr. Holian's protracted illness, the Board accepted his resignation, to be effective July 1, 1955, and, at the same time, it was voted that we express our appreciation to him for all his services to the Society.

The Board then gave Miss Anne Zino, Assistant Business Manager, who has been handling the duties of the Assistant Secretary for the last year, a vote of confidence.

The meeting was adjourned at 3:20 P.M.

HENRY B. LINFORD, *Secretary*



M. J. PRYOR

Young Author's Prize

At the Annual Banquet held on Tuesday evening, May 3, during the Cincinnati Meeting of the Society, it was announced that the winner of the Young Author's Prize of $100 was M. J. Pryor, Kaiser Aluminum and Chemical Corporation, Spokane, Wash., for his paper "The Protective Action of Pigments on Steel" which appeared in the March 1954 issue of the JOURNAL.

Dr. Pryor received his technical education in Cambridge, England, where he was graduated with honors in metallurgy from Cambridge University in 1946. In 1949 he received his M.A. and Ph.D. after studying with Dr. U. R. Evans at the same institution. Subsequently, Dr. Pryor held a post doctorate fellowship at the National Research Council of Canada where he later became a Research Officer. In 1953 he joined the staff of Kaiser Aluminum's Department of Metallurgical Research as a Research Metallurgist in the Corrosion Section.

He is the author of nearly 20 scientific papers dealing mainly with corrosion and electrochemical mechanisms. Dr. Pryor's main areas of research have been in the mechanisms of inhibition of the corrosion of iron and in the properties of surface films on both iron and aluminum.

Turner Memorial Award to D. A. Vermilyea

D. A. Vermilyea, General Electric Company, Schenectady, N. Y., is the winner of the Francis Mills Turner Memorial Award, Sponsored by the Reinhold Publishing Corporation, consisting of $100 worth of books. His

D. A. VERMILYEA

paper entitled "Formation of Anodic Oxide Films on Cathodes" appeared in the August 1954 issue of the JOURNAL.

He received his B.S. degree in metallurgy from Rensselaer Polytechnic Institute in 1947. After working for DuPont for one year, Dr. Vermilyea returned to Rensselaer as an instructor and while there took graduate courses. In 1951 he joined the staff of the General Electric Company's Research Laboratory. He received his Ph.D. degree from Rensselaer Polytechnic Institute in 1953.

Dr. Vermilyea has been concerned chiefly with the kinetics of the formation of thin films of reaction products on metals.

SECTION NEWS

Midland Section

On May 10, 1955, the Midland Section held a dinner in honor of Mr. V. V. Kendall, the speaker for the evening, at the Midland Country Club.

After dinner, the main program was held in the Dow Research Auditorium. Mr. Kendall, who is a well-known corrosion engineer with the National Tube Division of the United States Steel Corporation, gave a most interesting talk entitled "The Diagnosis of Corrosion Problems." Mr. Kendall had more than 45 colored slides to illustrate his lecture, as well as an exhibit of corrosion specimens. The specimens were varied in their origin and were representative of problems encountered over the past 30 years.

Examples of corrosion in radiant heating pipes, due to poor design and construction, were shown. Corrosion of pipe by oxygen, CO_2, and acids was illustrated, and means for diagnosing the type discussed. Cast iron graphitization and dezincification of brasses were discussed and illustrated.

PAUL R. JUCKNIESS,
Secretary-Treasurer

ROBERT I. JAFFEE

The third meeting of the season was held on May 24, with Dr. Robert I. Jaffee of Battelle Memorial Institute as guest speaker. Dinner in honor of Dr. Jaffee was held at the Midland Country Club. Dr. Jaffee spoke before an audience of about 100 in the Dow Main Auditorium. His talk was on "The Metallurgical Principles of Titanium Alloys."

He contrasted the physical metallurgical approach to titanium alloy problems at present with those of seven or eight years ago. Originally the concern was with equilibrium diagrams and tensile properties of alloys. Now, the kinetics of transformation and the dynamics of strain application are of major importance. Strain rates of interest range from those in creep tests to those found in impact. Stress concentration and possible embrittling effects of low temperatures are of increasing importance The effects of the alloying elements on the properties of alpha and beta solid solutions, and the interrelations between interstitial and substitutional solutes have been studied widely.

An interesting and extended discussion period followed Dr. Jaffee's remarks.

PAUL R. JUCKNIESS,
Secretary-Treasurer

The annual golf match between the Electrochemics and the Metallurgists, and the annual business meeting of the Midland Section were held on June 8. The Metallurgists won the match 7 to 6.

The following new officers were elected for the coming year:

Chairman—Marshall Neipert
Vice-Chairman—Paul Juckniess
Secretary-Treasurer—H. W. Schmidt
Representative on Council of Local Sections—Fred Koerker

Revisions to the local constitution were also made.

PAUL R. JUCKNIESS,
Secretary-Treasurer

New York Metropolitan Section

The May 18th meeting was our annual Ladies' Night, and 35 ladies were present. As usual, there were orchids for the ladies and other prizes for holders of the lucky numbers. The speaker for the evening was Dr. Maria Telkes, Project Director of the Solar Energy Program of the Research Division, New York University. Her topic was "Future Uses of Solar Energy."

While the sun supplies a tremendous amount of radiant energy to the surface of the earth, utilization of this energy for the purpose of producing high temperatures for distillation of water, cooking, the production of power, or other purposes has been made difficult by the manner in which it is diffused. Reflectors are usually required to direct the rays of the sun on the object to be heated. Where extremely high temperatures are desired, a large system of mirrors is necessary.

Perhaps the first use of solar energy was for the evaporation of sea water to obtain salt. At the time of the French Revolution, Lavoisier in France built a solar furnace which would melt even platinum. Since that time numerous attempts have been made to utilize solar energy. Furnaces have been built for the generation of steam power but the installation cost is high and power is only produced on sunny days, so these installations have not been entirely successful. There are some interesting possibilities of converting solar energy directly to electrical energy which might be stored. A series of thermocouples or thermopiles, or the recently developed solar batteries are methods which might be employed. Some solar furnaces are in use at the present time for obtaining very high temperatures. One such furnace located in the Pyrenees is 30 ft in diameter. During the war Dr. Telkes developed a small solar still which was

placed on life rafts to supply drinking water.

Solar stills are possibly the most promising field for the development of solar energy. The tropical areas of the world which receive the most solar energy are also deficient in fresh water. Some solar stills have been installed in northern Australia. Northern Africa and India are badly in need of fresh water and have an abundance of sunshine. Slides were shown of solar stills, one of which Dr. Telkes operated in Boston.

Dr. Telkes described a solar stove built in her laboratory, in which meals have been cooked on the roof of one of the New York University buildings. This device could be very useful in parts of India where fuel is scarce. Solar water heaters have been used in Florida but they have the disadvantage of working only during the time the sun is shining. There has been a great deal of interest in the use of solar energy for heating homes. So-called solar houses have been built in which the south side of the house was almost entirely of glass. In one, sunny weather these houses were overheated and in cold weather the loss of heat through the glass walls exceeded the heat utilized in more favorable weather. In order for solar heat to be utilized for house heating, some method had to be devised for storing energy which could be used when needed. Dr. Telkes has devised a system in which heat is stored as heat of fusion of some low melting, cheap, inorganic chemicals. Two such chemicals are suggested for this use. One is Glauber's salt and the other is sodium orthophosphate dodecahydrate. It has been found possible to heat a house in the latitude of Washington, D. C., by this method. The speaker showed a most interesting group of slides depicting various applications of solar heating.

KENNETH B. MCCAIN,
Secretary-Treasurer

At its annual business meeting on May 18, the Metropolitan Section elected the following officers for the year 1955–1956:

Chairman—Myron B. Diggin
Vice-Chairman—Cecil V. King
Secretary-Treasurer—Kenneth B. McCain, Wilbur B. Driver Co., 1875 McCarter Highway, Newark 4, N. J.
Executive Committee—Bernard Agruss, Mrs. Frances Lang, and Gunnar Stendahl

Martin F. Quaely was appointed to a two-year term on the Council of Local Sections; H. Bandes has an additional year to serve; F. A. Lowenheim will also remain a member of the Council for another year until his term of office on the Board of Directors of the Society expires.

KENNETH B. MCCAIN,
Secretary-Treasurer

Niagara Falls Section

Ladies' night was held at the Red Coach Inn on May 11.

Dr. G. Butler presented the following slate of Niagara Section Officers who were elected without dissenting vote:

Chairman—John Currey
Vice-Chairman—R. B. MacMullin
Secretary-Treasurer—L. A. Stoyell

An Alco representative with 47 years' experience in the aluminum industry, Mr. C. P. Monteith, gave an interesting talk on "The Kitimat Story." An impressive technicolor film of the four major phases of this undertaking was shown.

Following the meeting, a letter was sent to Mr. Eric F. West of the Aluminum Company of Canada thanking them for their services.

L. A. STOYELL, *Secretary*

Pacific Northwest Section

The March meeting of the Pacific Northwest Section was held Tuesday, March 29, at Rose's Highway Inn, midway between Seattle and Tacoma, Wash. Sixteen members and guests were privileged to hear a talk by Dr. M. J. Pryor, who is at present in charge of the Metallurgical Corrosion Group of the Kaiser Aluminum and Chemical Corp. in Spokane, Wash. Dr. Pryor's topic was "The Mechanism of Anodic Inhibition of the Corrosion of Steel."

First reviewing the absorption and precipitation theories of film formation on iron, Dr. Pryor discussed research work he had done at Cambridge under Dr. U. R. Evans, which showed the important role of dissolved oxygen in solutions inhibited with various anions. Electron diffraction techniques revealed that the films formed were gamma iron oxide rather than hydrated oxides. Postulation of the formation of the gamma oxide is supported by the fact that the films tend to be insoluble in acid media. It was also shown that in chromate inhibited solutions, within the limits of accuracy of the technique employed, there was no evidence of the presence of chromic hydroxide. The stoichiometry would indicate that if the chromate were reduced in the formation of the oxide film, approximately 60% of chromic hydroxide should be present. Using these findings as a basis for postulating the formation of a film of the gamma oxide, the role of the inhibitor in maintaining a continuous film was explained.

Dr. Pryor's research indicated that in gamma oxide films formed in sodium hydroxide solution, inclusions in the films had been noted which were of the order of 4 to 5 times thicker than the balance of the surface film. These were apparently the results of discontinuities in the protective film, which had been plugged by the normal corrosion products of iron, the hydrated oxide.

Weight loss and polarization curves were presented which showed the effects of aeration and *p*H on solutions inhibited with anions such as the phosphates, silicate, acetate, and benzoate. In the absence of oxygen, corrosion was not stopped, as shown by low but detectable rates of corrosion. As the solutions were made more alkaline, corrosion decreased and the equilibrium potential changed by about 0.59 mv per *p*H unit. Phosphate inhibited solutions were an exception, probably because film repair by formation of ferric phosphate plugs would be favored in low *p*H solutions.

As the film of gamma oxide (similar in all characteristics to those formed in air) is established, the diffusion of ferrous ion is gradually retarded and, as long as film repair can be maintained, corrosion is stopped. At discontinuities, repair is usually effected by the formation of plugs of the hydrated oxides.

In solutions inhibited with nitrate or chromate, both of which it was shown inhibit in the absence of dissolved oxygen, film repair may be postulated to be the result of formation of plugs of FeO accompanied by reduction of the inhibiting anion. Under these conditions it would be logical to expect that the plugs, only, would contain the stoichiometric quantity of chromium resulting from the reduction of the chromate ion, or that ammonia might be released as a result of the reduction of the nitrate.

KENNETH L. SANBORN,
Secretary-Treasurer

Philadelphia Section

The Philadelphia Section concluded its 1954–1955 season with a very enjoyable meeting at Swarthmore, Pa. Over 50 members, guests, and wives gathered for cocktails at the attractive and spacious home of Dr. and Mrs. Knut Krieger. The fair weather made it pos-

sible to enjoy this portion of the program on the terrace and in the garden. The group then repaired to the dining hall of Swarthmore College for dinner. Many of those in attendance had come to the campus before the cocktail hour to stroll about and inspect the beautiful plantings.

After dinner, the Section moved to the lecture hall of the Chemistry Building to hear a talk by Dr. Charles C. Price entitled "Science, Power, and Freedom." Dr. Price is a graduate of Swarthmore College and of Harvard University. He has been on the staff of the University of Illinois, head of the Chemistry Department at the University of Notre Dame, and is now Blanchard Professor of Chemistry and head of the Department of Chemistry at the University of Pennsylvania. Dr. Price has perhaps become as well known for his active interest in national and international affairs as for his numerous contributions to chemistry. His stimulating talk on this occasion was an earnest and compelling exposition of his views on current international problems, and was enthusiastically received by the audience.

Section officers elected for the coming year were:

Chairman—Edgar L. Eckfeldt
Vice-Chairman—G. Franklin Temple
Treasurer—Albert A. Ware
Secretary—George W. Bodamer

G. W. Bodamer, *Secretary*

San Francisco Section

The last meeting of the current year was held on May 25 at the Faculty Club, University of California, Berkeley, and was attended by 25 members and guests.

A short business meeting preceded the regular one. A report was presented on the last national convention, and a progress report was made covering the arrangements for the Spring 1956 session to be held in San Francisco. The present officers were reelected for the 1955–1956 fiscal year. They are listed below:

Chairman—Charles W. Tobias
Vice-Chairman—Morris Feinleib
Secretary—Henry F. Myers, Columbia-Geneva Steel Co., Russ Bldg., San Francisco, Calif.
Treasurer—Ray A. Zimmerly
Representatives on Council of Local Sections—Richard F. Bechtold and Sam H. Dreisbach

Following this, Mr. Ralph Brogie, who represents the Brown Instrument Division of the Minneapolis-Honeywell Regulator Co., gave an excellent talk on the use of electronic potentiometers in industry.

Mr. Brogie traced the development of this type of instrument from the early millivoltmeter movements down to some of the latest scanning, programming, and data-handling electronic systems. He demonstrated how these electronic potentiometers could be applied to systems which furnish their own electrical potentials, as well as to those which did not. Changes in flow, or pressure for instance, could be converted to electrical potentials through transducers and then fed into electronic potentiometers. The use of scanners to read a large number of points in a short interval, as well as to mark those exceeding a preset limit, was illustrated. Data-handling systems, which could be arranged to type the results into a fixed form, were briefly discussed. It was illustrated that this system could type a form, as well as transmit the data to several other locations via teletype setups, where a similar data-handler would then reproduce the original form. Some features of completely automatic control were also mentioned.

The maintenance problem, which becomes a serious limitation, was outlined. Mr. Brogie indicated that one solution was to replace specified mechanical parts at set time intervals, for this is the seat of most of the trouble in these electronic instruments.

A very good movie made by the DuPont Co., entitled "Utilization of Modern Electronic Potentiometers in Research," was shown by Mr. Brogie, who then consented to answer questions from the audience. A lively question and answer period followed.

Bernard Porter

Washington-Baltimore Section

The 33rd technical meeting of the Section was held at the National Bureau of Standards on May 26. Dr. Mortimer C. Bloom of the Naval Research Laboratory described a hydrogen effusion method for measuring corrosion rates at high temperatures and pressures.

The specimens used in this work were capsules of mild or stainless steel fabricated from ¼ in. tubing. The tubes, filled with the corroding solution, were crimped, and cut into short lengths. Spot welding completed the seal of the capsule, which was suspended in the apparatus on a platinum wire terminated by steel balls. The apparatus consisted of an evacuated Pyrex glass system, a portion of which was enclosed in a furnace. The specimen was lowered into the heated area with a magnet.

A system of gauges measured the hydrogen pressure developed during the course of the reaction. This pressure arose from the hydrogen diffusing through the walls of the specimen. The pressure, or amount of hydrogen, may be recorded at any time interval desired, thus providing a measure of the corrosion at any given time, rather than the total corrosion of individual specimens as in common gravimetric methods.

Dr. Bloom presented some of the data obtained by this method on carbon and stainless steels reacting with alkaline media at elevated temperatures. The results show a remarkable reproducibility, and indicate that this new technique promises to yield valuable information on the kinetics and mechanisms of corrosion processes.

The following officers were elected for 1955–1956:

Chairman—Fielding Ogburn
Vice-Chairman—D. T. Ferrell, Jr.
Treasurer—Gwendolyn B. Wood
Secretary—Jeanne Burbank
Representatives on Council of Local Sections—J. C. White and D. T. Ferrell, Jr.

Jeanne Burbank, *Secretary*

PERSONALS

Henry Mahlstedt has been named Manager of Sales of the Electroplating and Coating Sales Department of Metal & Thermit Corp. He has been connected with associated companies of Metal & Thermit since 1927, and for the past seven years was sales manager of the plating department of United Chromium, Inc.

B. A. Daley has been promoted to Chief Engineer of the Defense Division of Servel, Inc., Evansville, Ind. Mr. Daley previously was chief metallurgist. Servel's defense activities include the manufacture of wings, spars, and other aircraft components.

Bernard Kopelman was recently appointed Chief Engineer of the Atomic Energy Division of Sylvania Electric Products Inc., Bayside, N. Y. Dr. Kopelman will be responsible for all technical operations, including research and development of atomic fuel elements and reactor components.

WARREN D. SHERROW has been advanced from Special Sales Representative to Product Manager of Anodes, Electrode Division, Great Lakes Carbon Corp. His headquarters remain in the Electrode Division's sales office at Niagara Falls, N. Y.

FRED J. KIRKMAN

FRED J. KIRKMAN AND JOSEPH J. COLEMAN have been promoted to Executive Vice-President and Vice-President of Engineering, respectively, of the Burgess Battery Co., Freeport, Ill. Mr. Kirkman was formerly Vice-President and General Manager. Dr. Coleman had been the company's Chief Engineer.

JOSEPH J. COLEMAN

RALPH ROBERTS, formerly with the Office of Naval Research in Washington, D. C., has transferred to the London office of ONR.

R. H. J. CREIGHTON, J. HALPERN, AND W. G. WALLACE were among 52 prominent chemists and chemical engineers elected as Fellows of The Chemical Institute of Canada. Their election was announced at the 38th Annual Conference of the Institute on May 30. This honor is granted each year to a few members of the Institute in recognition of their contributions to Canadian chemistry and chemical engineering.

RAY HILL WHITE

Ray Hill White, Emeritus Member of The Electrochemical Society, died on June 15, 1955 in his home at Summerville, S. C. He was 76 years old.

The son of Reverend James William White and Ellen Margaret Hill, R. H. White was born in Maine, Broom County, N. Y., on July 1, 1879. He graduated from Rochester University in 1901 and from the Massachusetts Institute of Technology, where he studied electrochemistry, in 1905.

Mr. White was research engineer for the Barium Company and then the Norton Company at Niagara Falls, N. Y. Later, he became a vice-president of the Simonds Saw & Steel Company, in charge of their abrasive industry, in Philadelphia, Pa., Hamilton, Ontario, and Arvida, Quebec, having designed, built, and managed the Arvida Plant. He retired in 1945, being retained three years longer in an advisory capacity.

He also did research work in New York City and for the Lachwana Steel Company in Buffalo, N. Y., and the Pennsylvania Salt Company, in Natrona, Pa.

In addition to The Electrochemical Society, which he joined in October 1902, Mr. White was a member of the Grinding-Wheel and Abrasive Grain Society.

He is survived by his wife, Frances French White; a half-sister, Mrs. Harris Dale Hineline; her daughter, Patricia Frances Hineline; and three nephews.

One well-deserved tribute was paid to Mr. White some years ago when an acquaintance said to him, "You have the highest ideals, and live up to them, of any person I ever have known."

NEW MEMBERS

In June 1955 the following were approved for membership in The Electrochemical Society by the Admissions Committee:

Active Members

CHARLES S. BAUGMAN, National Carbon Research Labs.; Mail add: 11211 Hessler Rd., Cleveland 6, Ohio (Theoretical Electrochemistry)

PAUL G. BENIGNUS, Monsanto Chemical Co.; Mail add: 6518 W. Main St., Belleville, Ill. (Electric Insulation)

ALI RIZA BERKEM, University of Istanbul; Mail add: Fen Fakültesi, Istanbul, Turkey (Theoretical Electrochemistry)

WALTER J. BERNARD, Sprague Electric Co.; Mail add: Box 132, Williamstown, Mass. (Theoretical Electrochemistry)

ALVIN BEYLER, JR., National Video Corp.; Mail add: 4300 W. 47 St., Chicago, Ill. (Corrosion, Electrodeposition, Electronics, Electro-Organic, Industrial Electrolytic)

WILLIAM E. BRADLEY, Philco Corp., Research Div., Tioga & C Sts., Philadelphia 34, Pa. (Electronics)

ROBERT A. BURESCH, Titanium Alloys Div., National Lead Co.; Mail add: 8505 Krull Pky., Niagara Falls, N. Y. (Electrothermics & Metallurgy)

JOHN G. CASHELL, Mellon Institute of Industrial Research; Mail add: 4400 Fifth Ave., Pittsburgh 13, Pa. (Electronics)

CECIL G. CHADWICK, Electro Metallurgical Co.; Mail add: 110 Meadowbrook Dr., Lewiston, N. Y. (Electrothermics & Metallurgy)

JOSÉ G. PÉREZ DEL RÍO, Escuela de Peritos; Mail add: c/Leopoldo Alas 25-Gijón, Spain (Electrodeposition, Industrial Electrolytic)

V. J. DE SANTIS, General Electric Co.; Mail add: 1079 Parkwood Blvd., Schenectady, N. Y. (Electronics)

ROSTISLAV DIDTSCHENKO, National Carbon Co., Research Labs., P. O. Box 6087, Cleveland, Ohio (Industrial Electrolytic, Theoretical Electrochemistry)

STEPHEN V. DILLON, Johns-Manville Sales Corp.; Mail add: 15-A W. 64 St., New York 23, N. Y. (Electric Insulation)

BINETTI GIULIO, Centro Ricerche Metallurgiche, Corso Matteotti, 3 bis, Torino, Italy (Battery, Corrosion, Electrodeposition, Electrothermics & Metallurgy, Industrial Electrolytic)

OTTMAR A. HAMMELMANN, Sonotone Corp., Battery Improvement Lab., Elmsford, N. Y. (Battery)

VIRGIL L. HANSLEY, National Distillers Products Corp.; Mail add: 4900 Burley Hills Dr., Cincinnati 27, Ohio (Electrothermics & Metallurgy, Industrial Electrolytic, Theoretical Electrochemistry)

ARTHUR D. R. HARRISON, Aluminium

Nonmember Journal Subscribers

Nonmember subscription rates to the JOURNAL in 1956 will be $18.00 instead of the $15.00 previously charged. Current subscribers will be mailed invoices for $18.00 late in September.

Laboratories Ltd.; Mail add: 159 Lawrie, Arvida, Que., Canada (Electrodeposition, Electrothermics & Metallurgy, Industrial Electrolytic, Theoretical Electrochemistry)

WILLIAM W. HEILMAN, Electro-Metallurgical Co.; Mail add: River Rd., Youngstown, N. Y. (Electrothermics & Metallurgy)

CARL HERING, U. S. Naval Postgraduate School; Mail add: P. O. Box 203, Corvallis, Oreg. (Electrothermics & Metallurgy)

MICHAEL F. LAMORTE, Signal Corps Engineering Labs.; Mail add: R.F.D. 1, Box 333A, Belmar, N. J. (Electronics)

SIMON LARACH, RCA Labs., Princeton, N. J. (Electronics)

DAVID K. LEWIS, The Radio Valve Co., Ltd.; Mail add: 885 Melton Dr., Applewood Acres, Port Credit, Ont., Canada (Electronics)

DAVID A. LUPFER, General Electric Co., Bldg. 3, Rm. 16, Electronics Park, Syracuse, N. Y. (Electric Insulation)

JOHN W. LYNN, Carbide and Carbon Chemicals Co.; Mail add: 317 Viola Rd., Charleston 4, W. Va. (Electro-Organic)

WILLIAM H. MAGRUDER, Electrometallurgical Co.; Mail add: 526–81st St., Niagara Falls, N. Y. (Electrothermics & Metallurgy)

LEONARD MAISEL, National Union Electric Corp., 350 Scotland Rd., Orange, N. J. (Electronics)

RICHARD S. MARGESON, Speer Carbon Co., International Graphite Div.; Mail add: 1309 Roselle Ave., Niagara Falls, N. Y. (Industrial Electrolytic)

BERTRAM MAY, May Machine Co., Inc., 195 Chrystie St., New York 2, N. Y. (Battery)

OLIVER W. MOLES, Titanium Div., National Lead Co.; Mail add: R.F.D. 3, Plainfield, N. J.

RALPH MOON, Sangamo Electric Co.; Mail add: 1015 N. Market St., Marion, Ill. (Electric Insulation)

RAYMOND J. MOULY, Quebec Iron & Titanium Co.; Mail add: 53 George St., Sorel, Que., Canada (Electrothermics & Metallurgy)

EMIL NENNIGER, Surveyor, Nenniger & Chênevert; Mail add: 1440 St. Catherine St., West, Room 1012, Montreal, P. Q., Canada (Electrothermics & Metallurgy, Theoretical Electrochemistry)

EDWARD C. OLSON, Physics Dept., The Upjohn Co., Kalamazoo, Mich. (Electro-Organic)

EDGAR A. PETT, The Norton Co.; Mail add: 3350 McLeod Rd., RR No. 2, Niagara Falls, Ont., Canada (Electrothermics & Metallurgy)

CARL E. RUDIGER, P. R. Mallory & Co., Inc.; Mail add: 522 Sherman Ave., Hawthorne, N. Y. (Battery)

STEPHEN W. SCOTT, Electrometallurgical Co.; Mail add: 1097–98th St., Niagara Falls, N. Y. (Electrodeposition)

JOSEPH H. SULLIVAN, Olin Mathieson Chemical Corp.; Mail add: 2834 Lewiston Rd., Niagara Falls, N. Y. (Industrial Electrolytic)

BENSON R. SUNDHEIM, New York University, Washington Square College, Washington Square 3, N. Y. (Theoretical Electrochemistry)

ALFRED F. TORRISI, Ohmite Manufacturing Co.; Mail add: 1232 W. Sherwin Ave., Chicago 26, Ill. (Electric Insulation)

MARCEL TROTTIER, Quebec Iron & Titanium Corp., P. O. Box 40, Sorel, P. Q., Canada (Electrothermics & Metallurgy, Theoretical Electrochemistry)

CHARLES H. WEAVER, Electro Metallurgical Co., Niagara Falls, N. Y. (Electrothermics & Metallurgy)

JOSEPH R. WICKHAM, Superior Electronics; Mail add: 11 N. York St., Paterson, N. J. (Electronics)

JOHN E. YARMACK, Lorain Products Corp.; Mail add: 3952 E. Lake Rd., Lorain, Ohio (Electronics)

ECS Membership Statistics

The following two tables give breakdown of membership as of July 1, 1955. 73 delinquents were removed from the rolls as of May 1, 1955. The Secretary's Office feels that a regular accounting of membership will be very stimulating to membership committee activities. In Table I it should be noted that the totals appearing in the right-hand column are *not* the sums of the figures in that line since members belong to more than one Division and, also, because Sustaining Members are not assigned to Divisions. But the totals listed are the total membership in each Section. In Table I, Sustaining Members have been credited to the various Sections.

TABLE I. *ECS Membership by Sections and Divisions*

Section	Division												
	Battery	Corrosion	Electric Insulation	Electrodeposition	Electronics	Electro-Organic	Electrothermics & Met.	Industrial Electrolytics	Theoretical Electrochem.	No Division	Totals as of 7/1/55	Totals as of 1/1/55	Net Change
Chicago	9	28	3	43	11	8	9	10	16	15	99	102	−3
Cleveland	42	37	4	46	30	8	18	27	43	16	166	150	+16
Detroit	5	15	6	33	6	7	4	2	19	20	70	67	+3
India	5	2	1	9	3	4	2	8	6	3	22	23	−1
Midland	5	12	0	3	1	2	6	15	6	4	36	36	0
New York	60	100	18	130	62	25	46	52	76	73	411	374	+37
Niagara Falls	6	19	0	15	2	6	44	43	12	26	126	105	+21
Pacific Northwest	4	10	0	8	1	2	3	12	12	5	35	29	+6
Philadelphia	19	27	4	39	39	18	18	13	46	29	159	144	+15
Pittsburgh	3	27	3	21	7	5	19	14	25	12	77	69	+8
San Francisco	7	10	1	12	6	3	7	18	11	3	41	38	+3
Washington-Baltimore	33	36	10	33	18	3	12	12	28	7	110	104	+6
Ontario-Quebec	7	11	0	12	0	3	22	19	4	13	57	43	+14
U.S. Nonsection	66	145	23	153	80	48	90	95	134	102	607	581	+26
Foreign Nonsection	29	38	6	41	14	21	25	46	49	57	166	176	+10
Total as of 7/1/55	300	517	79	598	280	163	325	386	487	385		2182	
Total as of 1/1/55	281	516	81	590	276	169	309	374	460	306	2141		
Net Change	+19	+1	−2	+8	+4	−6	+16	+12	+27	+79			

TABLE II. *ECS Membership by Grade*

	Total as of 7/1/55	Total as of 1/1/55	Net Change
Active	1939	1889	+50
Life	14	14	0
Emeritus	36	39	−3
Associate	48	63	−15
Student	40	31	+9
Honorary	5	5	0
Sustaining	100	100	0
Total	2182	2141	+41

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DAN G. SOLTIS, National Carbon Co.; Mail add: 1800 Pleasantdale Ave., Cleveland 9, Ohio (Battery)

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CHARLES A. GUDERJAHN, University of Cincinnati; Mail add: 1850 Chaucer Dr., Cincinnati 37, Ohio (Electronics)

SAMI A. HALABY, University of Cincinnati; Mail add: 1521 Teakwood Ave., Cincinnati 21, Ohio (Theoretical Electrochemistry)

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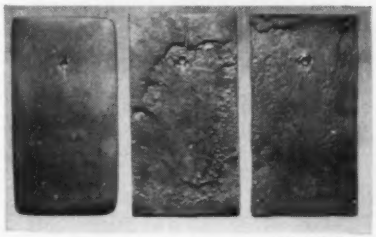

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LETTERS TO THE EDITOR

A New Simple Method for Conversion of Silver Cyanide to Silver Sulfate for Analysis

Dear Sir:

The method for analysis of silver plating solution described in "Modern Electroplating"[1] always leaves a trace of undissolved silver cyanide which thus is not available for titration. As a result, some chemists[2] recommend precipitation of silver as silver sulfide, then filtration, followed by the above method.

Being reluctant to expend any more time or work than necessary, I have worked out a new method for this determination, as follows:

1. Place 10 ml of plating solution in a clean 400 ml Pyrex beaker and heat to dryness at about 200°F. In this laboratory, a regular laboratory hotplate is used at low heat and the beaker is protected further with a porcelain plate. Popping will spoil the sample. When dryness is obtained, bake at high enough temperature to cause a slight browning of the residue in the beaker. Usually this can be accomplished in the time required for other determinations on the sample.

2. Measure into a 50 ml graduate, 20 ml of *fuming nitric acid* and 10 ml of concentrated sulfuric acid. (This may be frowned upon by fearful people, but I have done it many times. The mixture does not heat or misbehave.) Pour this at once (quickly) into the beaker containing the silver residue. *Good ventilation is essential* at this point. As soon as the strong ebullition subsides, place directly on hotplate at medium heat.

[1] "Modern Electroplating," The Electrochemical Society, Inc., New York (1942).

[2] Private communication.

At this point, it should be evident that the silver has all dissolved, and the solution will be slightly green. Continue heating to strong fumes of sulfuric acid.

3. Cool the solution of silver sulfate, add 250 ml of distilled water, and heat to boiling, if necessary, to dissolve any undissolved solids. Cool this solution and titrate with sodium thiocyanate and ferric ammonium alum, according to standard procedures.

Notes on accuracy.—I have run numerous determinations against silver nitrate and against silver nitrate plus sodium cyanide, treated in the above manner. There was no discernable difference in the quantitative titration. This probably works because the cyanide is removed with heat and oxidation in the absence of water.

Ordinary concentrated nitric acid will not work! Unfortunately, the above will not work if the fuming nitric acid and sulfuric acid are not added *together* to a heated residue.

FOSTER H. POLAND
Chautauqua Specialties Co.
Greenhurst, N. Y.

Dear Sir:

I read with interest Dr. F. A. Lowenheim's Letter to the Editor in the May issue of the JOURNAL. If you will recall, Professor Eckstein at the Society luncheon in Cincinnati opened his talk with a very similar remark, namely, that all physiology is essentially electrochemistry. What is meant is, of course, that in biochemical processes physicochemical—largely electrochemical—phenomena in the body fluids, cell interiors, and cell membranes play an important role. While I realize that Dr. Lowenheim's suggestion was meant facetiously, it could be turned into a more serious one; a division for biochemistry could be organized, increasing both membership and JOURNAL subscription.

ANDREW GEMANT
The Detroit Edison Co.
Detroit, Mich.

ECS Meetings

The Fall Meeting of the Society will be held October 9 to 13, 1955 at the Hotel William Penn, Pittsburgh, Pa.

Sessions are scheduled on Batteries, Corrosion, Electrodeposition, Electronics—Semiconductors, Electro-Organics, and Electrothermics and Metallurgy.

The Spring Meeting of the Society will be held April 29 to May 3, 1956 at the Mark-Hopkins Hotel, San Francisco, Calif.

Triplicate copies of abstracts (not exceeding 75 words in length) of papers for the San Francisco Meeting must reach the Secretary's office, 216 West 102nd St., New York 25, N. Y., *not later than January 2, 1956* in order to be included in the program.

Sessions will be scheduled on Electric Insulation, Electronics (including Luminescence, Oxide-Cathodes, Phosphor Application, Semiconductors, and Instrumentation), Industrial Electrolytics, and Electrothermics and Metallurgy, and probably Theoretical Electrochemistry.

Triplicate copies of manuscripts are acceptable either before or after presentation of a paper at a meeting. There is no connection between presentation of papers and publication in the JOURNAL.

"Vapor Plating"

"Vapor Plating; The Formation of Coatings by Vapor-Deposition Techniques," by C. F. Powell, I. E. Campbell, and B. W. Gonsor, sponsored by The Electrochemical Society, and published by John Wiley & Sons, Inc., is now available.

This critical and authoritative review of the applications and techniques of vapor deposition of metals and nonmetals is the first single source of reference for data and information on these processes.

The book is being sold for $5.50 by John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. Members of the Society who order the book through ECS Headquarters Office, 216 W. 102nd St., New York 25, N. Y., can receive a 33⅓% discount given to members. The publisher will mail the volume and invoice.

Brooklyn Polytech Symposium

The Polytechnic Institute of Brooklyn, as one of its series of Centennial Symposia, is holding a Symposium on "Electroluminescence and Photoconduction in Organic Phosphors," September 9 and 10, 1955. Inquiries should be directed to Professor J. J. Dropkin, Polytechnic Institute of Brooklyn, 85 Livingston St., Brooklyn 1, N. Y.

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DECEMBER 1955 DISCUSSION SECTION

A Discussion Section, covering papers published in the January–June 1955 JOURNALS, is scheduled for publication in the December 1955 issue. Any discussion which did not reach the Editor in time for inclusion in the June 1955 Discussion Section will be included in the December 1955 issue. Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the Managing Editor of the JOURNAL, 216 West 102nd Street, New York 25, N. Y., not later than August 15, 1955. All discussions will be forwarded to the author, or authors, for reply before being printed in the JOURNAL.

DEX

. 203C
. 191C
Cover 4
. 180C
-
Cover 2
. 184C
. 181C
. 183C
ts
. 186C
nt
. 182C

receive a
bers. The
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Kinetics of Nickel-Sulfur and Steel-Sulfur Reactions[1]

ANDREW DRAVNIEKS

Engineering Research Department, Standard Oil Company (Indiana), Whiting, Indiana

ABSTRACT

The reaction of nickel with molten sulfur between 205° and 445°C follows the parabolic law. Up to 260°C the millerite form of NiS was the only sulfide detectable in the scale. At 340°C and higher, the high temperature B8 form of NiS was the only sulfide in the scale. The activation energy (Arrhenius) below approximately 300°C is in excess of 50 kcal; above this temperature, it is about 20 kcal. This compares with an activation energy of 41 kcal for the iron-sulfur reaction over the entire temperature range, where only one FeS form is known. Ni_3S_2, Ni_6S_5, two forms of NiS, and NiS_2, but not Ni_7S_6 and Ni_3S_4, were found to form upon exhaustive reaction of the corresponding mixtures of Ni and S. Formation of NiS_2 was several thousand times slower than the formation of NiS. NiS formed continuously. In the formation of FeS, definite evidence of scale failures and healings was found. A formal description of such a scale growth law is given and a term "microcataclysmic" is proposed to describe this form of kinetics.

INTRODUCTION

Nickel and some nickel alloys are known to be susceptible to attack by sulfur compounds. Relatively little is known, however, about the kinetics of nickel sulfide formation, especially in the moderately elevated temperature range. The present work was undertaken to obtain such kinetic data and to compare them with the kinetics of iron sulfide formation, investigated previously (1), together with some newer data. To avoid complications arising from the presence of foreign species, formation of sulfides was studied in a molten sulfur medium.

EXPERIMENTAL WORK AND RESULTS

The experiments were conducted by two methods.

In the first method, triplicate samples of A-nickel (45 × 8 × 0.62 mm) were immersed in molten sulfur at several temperatures for various periods of time. Nominal composition of this nickel was given as: 99.4% Ni, 0.1% Cu, 0.15% Fe, 0.2% Mn, 0.05% Si, and 0.10% C. The nickel content includes less than 1% cobalt. When specimens were removed from the sulfur, they were quenched in water. Weight loss was determined after mechanical removal of the sulfidic scale. A short pickling in 10% sulfuric acid was helpful in facilitating scale removal. Averages from the triplicate specimens were used for the reaction-time curves, drawn as the top portion of Fig. 1 on the basis of the parabolic law.

In the second method, the electrical conductivity of nickel strips immersed in molten sulfur was followed with time. Specimens were made of 0.025 mm (0.001 in.) A-nickel sheet. The technique and interpretation of the measurements have been described elsewhere (1, 2). The electrical conductivity of nickel sulfides is quite high, so that, even after the total disappearance of the nickel metal by conversion to an initial form of sulfide, the specimen still has considerable conductivity. The sudden change in the slope of the plot of the relative conductivity vs. the square root of time, in the middle portion of Fig. 1, indicates the moment at which the metallic nickel phase disappears. This method indicated corrosion values somewhat higher than those indicated by weight loss measurements. However, since the samples of nickel used for the two techniques were of different thicknesses and origin, the discrepancy is readily explained.

At temperatures below 300°C corrosion becomes so slow that the weight loss method is no longer recommended because of the uncertainties involved in the removal of the sulfidic scale. The conductivity method gave an indication of the corrosion rate at a temperature as low as 210°C.

To determine whether any sulfur is dissolved by the metallic phase at lower temperatures, electrical conductivity-temperature curves were run on the nickel in the as-received condition, as well as on specimens which had been exposed to sulfur and the scale removed. The temperature coefficient was found to be unchanged after a 120-hr exposure to sulfur at 267°C. Thus, any appreciable solid solution of sulfur in nickel seems unlikely, at least at this temperature.

It was observed that, after the disappearance of the metallic nickel phase at about 445°C, additional, but slower, changes in the conductivity of the reaction product continued. To follow these changes, a small strip (10 × 2 × 0.025 mm) of A-nickel foil was fastened to the ends of four platinum wires and placed in boiling sulfur. Using the

[1] Manuscript received August 30, 1954. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

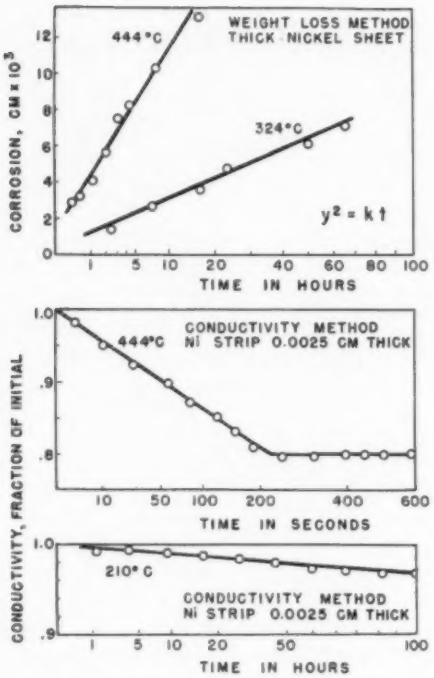

FIG. 1. Reaction of nickel with molten sulfur

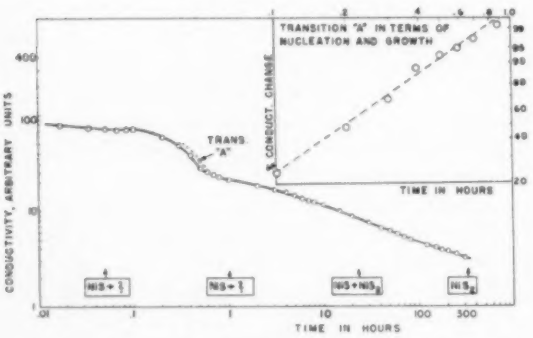

FIG. 2. Changes in electrical conductivity during sulfurization of a nickel strip 0.0025 cm thick at 444°C.

platinum leads and an appropriate circuit, a record of the electrical resistance of the specimen was obtained. The record is replotted in log-log coordinates in Fig. 2. The conductivity of the specimen followed a complex curve as sulfurization proceeded. The temperature coefficient of the conductivity was of a metallic type for the early products of reaction. With advancing sulfurization, a semiconducting component with a negative temperature coefficient accumulated, offsetting the influence of the primary product; its effect was most important below approximately 360°C.

In order to make an x-ray study of the reaction products, strips of nickel were withdrawn from sulfur into a fast flowing stream of argon. Scaled samples then were ground and were examined by powder x-ray methods. The patterns were compared with the Hanawalt-ASTM cards.

For metallographic examination, nickel strips 0.6 mm thick were reacted with sulfur kept at desired temperatures in thick Pyrex test tubes. After a completed exposure, the test tubes with specimens were rapidly cooled in a stream of air. Solid sulfur rods with the specimens embedded were cut and polished by the usual metallographic techniques. A 1-min etch in a mixture of freshly prepared 10% solutions of potassium cyanide and ammonium persulfate helped to differentiate the layers in the scale.

DISCUSSION

Kinetics of NiS *Formation*

From Fig. 1, the formation of nickel sulfides from nickel and molten sulfur follows the parabolic law between 210° and 444°C. Since a rate-limiting interface reaction seems unlikely in contact with molten sulfur, it appears safe to assume that the rate-limiting process is the diffusion through the sulfidic scale.

In the plot of log k vs. $1/T$ for the Ni + S reaction (Fig. 3) there is a change in slope in the vicinity of 300°C. The high temperature activation energy (Arrhenius) above 325°C is approximately 20 kcal; below 300° it is higher and may be given tentatively as 53 kcal. This compares with 41 kcal for the Fe + S reaction (1).

Farber and Ehrenberg (3) found parabolic kinetics in the sulfurization of nickel by 1% H_2S in CO or N_2 in the range 527°–1003°C. However, in these mixtures the rate-limiting interface reaction apparently interfered, as indicated by the dependence of the rate on the nature of the gas (CO or N_2). Similar indications are found in the work of Hauffe and Pfeiffer (4, 5), who were concerned with the formation of NiS at 670°C at reduced pressure of

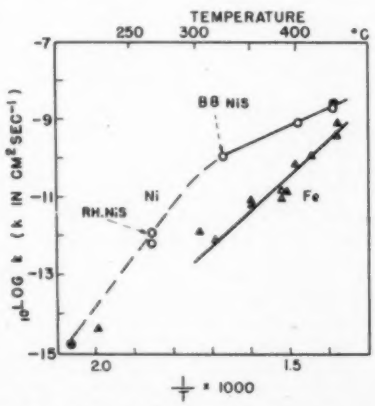

FIG. 3. Variation of Ni + S and Fe + S parabolic reaction rate constants with temperature. ○ ● Ni full: conductometric; △ ▲ Fe open: gravimetric.

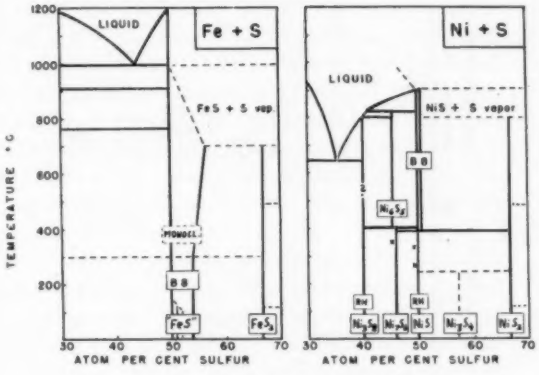

FIG. 4. Fe-S and Ni-S phase diagrams

sulfur vapor. On the other hand, Hauffe and Rahmel (5) found the parabolic law to hold for the formation of FeS at similar conditions in sulfur vapor. The activation energy for the latter case, as inferred from the plot in Hauffe's work, is not constant, however; its value approaches 23 kcal at 600°C, indicating that the reaction in sulfur vapor is not entirely diffusion controlled since in molten sulfur up to 445°C, where the surface reactions should be fast enough, E is 41 kcal.

It is best to discuss the kinetics on the basis of the nickel-sulfur and iron-sulfur phase diagrams, portions of which are reproduced in Fig. 4 [(6, 7), cf. also Ref. (18)]. As sulfurization proceeds, one should traverse the diagrams from left to right, with the final products being NiS_2 and FeS_2. As long as some metal is left, any or all intermediate sulfides may be present. The lowest sulfide would be next to the metal; the highest, however, not necessarily the NiS_2 and FeS_2, would be at the scale-sulfur interface. If interface reactions are disregarded, the thicknesses of individual sulfide layers would be proportional to diffusion rates in each sulfide (8, 9). If, in any of the sulfides, diffusion is very much slower than in others, this sulfide may be either missing or so disorganized as to escape detection in the x-ray or photomicrographic study. Furthermore, if surface reactions cannot be disregarded (4, 10), and the diffusion in one sulfide is sufficiently fast, the surface of such a sulfide, for example NiS, may be kept in such a condition by the rapid arrival of Ni ions that nucleation (11) of the next sulfide (NiS_2) may become impossible thermodynamically. Therefore, one does not necessarily expect to find in the scale all the sulfides listed in the phase diagrams if the metal-sulfur reaction is arrested while the metal is not fully consumed.

X-ray examination of the scale formed in the sulfurization of nickel showed the presence of the high temperature B8 form of NiS only from 340°C up. At 260°C, only the low temperature millerite form of NiS was found in the scale. No other sulfides were detectable. A metallographic examination revealed, however, that the scales were composed of three irregular layerlike components in each case. The arrangement found at 260°C differed from that found at higher temperatures. It seems possible that all three layers were NiS, with differences in the texture and composition (within the solid solution range) alone. This sort of thing has been observed, for instance, in copper iodide formed on copper in iodine vapor (12). Of course, it also is possible that some of the components may be Ni_3S_2 or Ni_9S_8 or NiS_2 in amounts and forms not detectable in the x-ray patterns.

In the present work (cf. Fig. 2) formation of NiS_2 was shown to be very slow. Difficulties in preparing nickel by the reduction of Ni_3S_2 (13) point out that, similarly, diffusion in Ni_3S_2 should be relatively slow, at least in the Ni-rich region of the Ni_3S_2 phase field.

Regardless of these further details, the change in the nickel-sulfur reaction kinetics in the vicinity of 300°C seems to be explained adequately by the two forms of NiS. The B8 form has a somewhat wider solubility range (6) and, therefore, is "looser" in terms of the forms of lattice disorder (14).

This accounts for the lower activation energy for the reaction in the range of existence of the B8 form. It should be noted, that, under the existing dynamic conditions of scale growth, the B8 form is encountered in the sulfide formed at temperatures well below 400°C, although this generally is considered to be the transition temperature between B8 and millerite under equilibrium conditions.

In the iron-sulfur system, the corresponding transition is missing. Although the "monoclinic" phase reportedly has been found in minerals, it is questionable if it forms in laboratory conditions (15–18). Hence, the activation energy is essentially constant.

Formation of Sulfides Other than NiS

When a NiS strip prepared by exhaustive sulfurization of nickel was kept in molten sulfur at 445°C (Fig. 2) nickel disulfide, NiS_2, was formed, at a very slow rate, as the final reaction product. From the rate of formation, diffusion in NiS_2 is several thousand times slower than in NiS. In the iron-sulfur reaction, FeS_2 formed much slower than FeS, approximately by a factor of one thousand (1, 5).

It is interesting to note that the conversion from NiS to NiS_2 is preceded by an intermediate transition ("A," Fig. 2). While all nickel phase is consumed, with formation of NiS, within 2–3 min, the transition "A" begins only after 10 min. X-ray patterns of the product before and after the transition are identical. Formation of NiS_2 to any detectable amount begins

much later, after several hours. Thus, the nature of the phase formed in the transition "A" is not clear. It may be noted that this transition appears to proceed by a sequence of saturation, nucleation, and grain growth, as indicated by the insert in Fig. 2. In the coordinates used, the above type of kinetics would result in a straight line plot. It may be speculated that after the total consumption of Ni metal, at 3 min, saturation of the primary NiS with more sulfur proceeds for several minutes until some sort of recrystallization begins, accompanied by a decrease in the electrical conductivity.

By milling together proper proportions of vacuum-redistilled sulfur and hydrogen-reduced nickel powder in evacuated containers[2] at various temperatures, Ni_3S_2, (13, 19–24), Ni_6S_5, (13, 18), both forms of NiS, and NiS_2, (24, 25), all with characteristic x-ray patterns, were prepared without difficulty. The transition between the B8 form of NiS and millerite was placed between 360° and 430°C, in accordance with the data by Lundquist and Rosenqvist (6, 18).

Ni_7S_6, (6, 26), did not form. Instead, at 340°C (compare crossmark on Fig. 4) Ni_6S_5 formed. Ni_3S_4 also did not form, even on prolonged milling; in the corresponding mixture at 210°C only NiS_2 and millerite were found. After these unsuccessful attempts, corresponding mixtures were pressed into pellets with several hundred atmospheres pressure and kept in evacuated capsules at temperatures for several months. No new patterns appeared.

The failure to find Ni_3S_4 is in agreement with the results of De Jong and Willems and others (27, 18), who also were unable to prepare it synthetically; Ni_3S_4 has been reported only as a mineral (27, 28). Thus, it was concluded that either the earlier literature data on the existence of Ni_7S_6 and Ni_3S_4 are in error or, more probably at least for the Ni_3S_4, they form extremely slowly and play no part in the main nickel-sulfur reaction kinetics.

Continuity of Scale Growth

There was no indication that breaks, blisters, or failures of any other type would interrupt the smooth parabolic growth of nickel sulfide scale.

However, in the Fe + S reaction, thin films grew parabolically whereas, in thicker films, sudden accelerations occurred. Fig. 5 shows a replotted record for the reaction of steel with molten sulfur at 270°C, obtained on a small specimen continuously by using the electrical resistance method. The upper

[2] 500 cem round bottom thick wall Pyrex centrifuge bottles, with a charge of ½ in. diameter porcelain balls. The milling crushes the scale on nickel or sulfide particles and accelerates the establishment of final equilibrium very considerably.

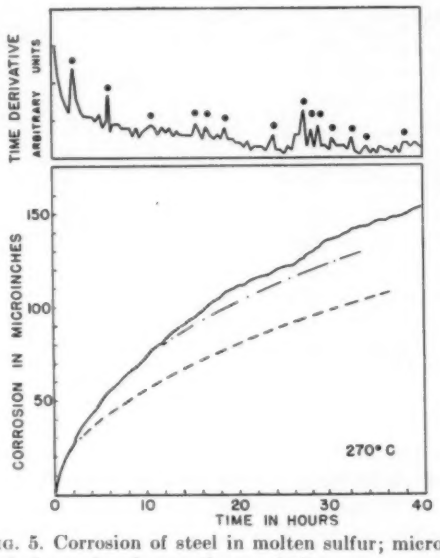

FIG. 5. Corrosion of steel in molten sulfur; microcataclysmic form of scale growth, $\bar{y} = kt^{n(t)}$.

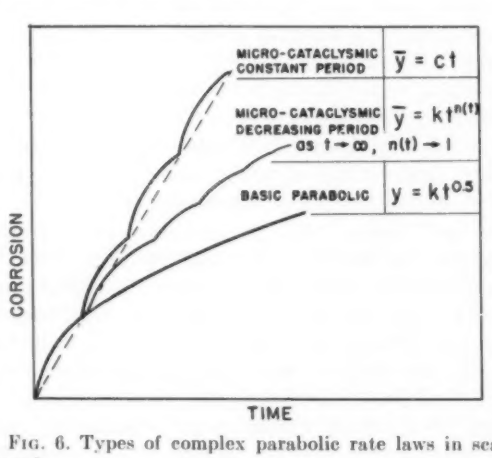

FIG. 6. Types of complex parabolic rate laws in scale growth.

plot represents differential rates of corrosion. The dots indicate periods of the fast accelerated growth where the acceleration was definitely larger than the resolution of measurements.

If the initial parabola were followed, as indicated by the broken curve, somewhat less reaction would have been expected. The experimental curve is never a parabola. The over-all shape is best described formally by the equation

$$\bar{y} = kt^{n(t)}$$

where $\bar{y}$ is the average corrosion, disregarding small inflections and $n(t)$ is a time function. For the ideal parabolic law: $n(t)$ = constant = 0.5. For the present case, $n(t)$ starts with 0.5 and keeps increasing.

At the same time, the empirical curve has a substructure of imperfect parabolas, each caused by a

localized failure in the scale such as cracking, peeling off, or open blistering followed by parabolic healing of the failure. The growth of an element of the scale is always basically parabolic, but is disturbed by ever-repeating microcataclysms. Related effects have been observed in the oxidation of metals (29, 30). It is proposed to denote such kinetics as the microcataclysmic scale growth. Fig. 6 schematizes the types of curves.

Here two functional parameters describe the kinetics. One is the basic parabolic constant k. This is a fundamental property of the chemical system concerned, and depends on the diffusivity through the corrosion product. The other is an undefined long term function $n(t)$. This depends on volume change in reaction, adherence, and mechanical properties of the product. At the same time it is highly dependent on the operational factors such as curvature of the surface, vibration, temperature constancy, etc. In an extreme case $n(t) = 1$, and this simplification is frequently used in industrial corrosion considerations.

The primary cause of the continuously occurring failures in the FeS scale may be the change in volume of scale as the amount of sulfur increases. Alsen (31), and Hägg and Suckdorff (32) showed that FeS shrinks as it takes up more S. This would build up stresses in the sulfide scale and tend to initiate failures.

Summary

Sulfurization of nickel by molten sulfur proceeds smoothly, without failures of the sulfidic scale. The reaction follows the parabolic law, but the activation energy changes in the vicinity of 300°C. The compound NiS was the only product found in the scale, and the change in the activation energy correlates with the change from the low temperature form of NiS to the high temperature form. In the sulfurization of iron the activation energy is constant, in agreement with absence of a phase transition. Higher sulfides such as NiS_2 and FeS_2 form much slower than the lower sulfides. It is doubtful if Ni_7S_6 and Ni_3S_4 exist. In the formation of FeS on steel in sulfur frequent sulfidic scale failures occur and the long-range kinetics are intermediate between the parabolic and linear. A term "microcataclysmic" is proposed to describe such kinetics.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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The Oxidation of Iron-Nickel Alloys[1]

R. T. Foley

General Engineering Laboratory, General Electric Company, Schenectady, New York

AND

J. U. Druck and R. E. Fryxell

Transformer Laboratories Department, General Electric Company, Pittsfield, Massachusetts

ABSTRACT

The high temperature (600°–900°C) oxidation of an iron-nickel alloy containing 42% nickel has been studied with the objective of formulating the mechanism of reaction. The rate was determined gravimetrically. Reaction products were examined by means of metallographic and electron diffraction techniques, as well as chemical analyses after stripping.

The temperature dependence of the parabolic oxidation rate constant follows the Arrhenius equation with the parameters dependent on the method of surface preparation. The oxide film, upon cooling, possesses a two-phase structure consisting of a nickel ferrite (next to the alloy) and Fe_2O_3. Differences in activation energies and oxidation rates are explained on the basis of diffusion through ferrite structures of a varying percentage of nickel.

Introduction

Iron and nickel form a continuous series of substitutional solid solution alloys, with both components oxidizable. While the kinetics of oxidation for alloys up to 30% nickel has been studied (1), no systematic investigation of alloys of about equal percentage of nickel and iron has been made in the 600°–900°C temperature range. Alloys of this type are used in making glass-to-metal seals so that a clear understanding of the kinetics and mechanism of oxidation is important in the electrical and electronic industry.

The most extensive study of the oxidation of iron-nickel alloys was made by Bénard and Moreau (1) who investigated the behavior of alloys containing 5, 10, 20, 30% Ni. The films developed on the alloys after oxidation and cooling to room temperature consisted of Fe_2O_3, Fe_3O_4, and a mixed layer of FeO and Fe_3O_4 (proceeding inward to the metal from the atmosphere). Koh and Caugherty (2) used an x-ray fluorescent technique to study the oxide layer formed on an alloy of 50 Ni–50 Fe composition. A spinel of lattice parameter a = 8.36 Å was identified along with weak lines for Fe_2O_3. Hickman and Gulbransen (3) followed the oxidation of 49 Fe, 49 Ni, 2 Mn alloy in purified O_2 at 1 mm pressure and from 300°–700°C by an electron diffraction method, the observation being made at temperature. A spinel with lattice parameter of 8.42–8.43Å was observed. This was assigned to Fe_3O_4 rather than to $NiFe_2O_4$ because of the slightly higher observed value.

The purpose of the present work was to study the kinetics of the oxidation of the iron-nickel alloy containing 42% Ni, and to formulate a mechanism of oxidation from the reaction rate and the nature of the surface layers. It was also desired to learn the influence of surface preparation on the kinetics and mechanism, with several "practical" surface preparations being included in the investigation.

Experimental

Metal preparation.—Strips of the iron-nickel alloy with an apparent surface area of 25.8 cm² were cut from a band which had been finally cold finished to a thickness of 0.051 cm. These strips were annealed and degassed in dry hydrogen (dew point = −50°F) for 2 hr at 1125°C, after which they were cooled in H_2 to about 75°C.

The chemical analysis of the alloy was: Fe = 57.4%; Ni = 41.8%; Si = 0.13%; Mn = 0.53%; C = 0.001%; Al = 0.05%; Co = 0.06%.

Various groups of samples received four different surface preparations before oxidation:

1. "As-rolled"—after annealing in hydrogen as described above, samples were swabbed with benzene and acetone, and dried before weighing. While these samples had a bright appearance, electron diffraction examination showed the presence, in faint but sharp pattern, of Fe_2O_3.

2. "Chemically cleaned"—the strip was pickled at 90°C for 2 min in an acid mixture made by dissolving one part by volume H_2SO_4 (95%), one part of HNO_3 (70%), and one part of HCl (37%) in nine parts of water. It was thoroughly rinsed, dipped in a mixture of two parts of H_2SO_4 and one of HNO_3, and again rinsed thoroughly. Samples were allowed

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to stand for about 1 hr in sodium cyanide solution (5 g/100 ml of solution) to neutralize any residual acid and again rinsed thoroughly. Finally, samples were rinsed in acetone and allowed to stand in acetone until used. Electron diffraction examination of this surface showed only the pattern corresponding to the iron-nickel alloy.

3. "Sand-blasted"—the as-rolled and annealed strip was sand-blasted with a sand characterized by a particle size range (90%) from 0.3 to 0.6 mm (diameters). Electron diffraction examination revealed the patterns for Fe_2O_3, and (possibly) Ni and Fe. These patterns were faint but sharp. No evidence of the sand remaining on the surface was seen in these patterns although analyses made after oxidation warranted the conclusion that the abrasive was embedded in the surface.

4. "Polished"—the annealed as-rolled strip was polished successively with Behr-Manning papers #240, #600, and #3/0, swabbed with benzene and acetone, and stored in acetone until used. Electron diffraction examination of a sample so polished and exposed to laboratory air gave the pattern of NiO. If the final polishing was carried out under kerosene, and if these two polishings were done with 3/0 and 4/0 paper successively, then only the Ni pattern was obtained.

It was apparent from the preliminary electron diffraction examination of the surface that the method of preparation affected not only the real surface area, but also the actual composition of the surface that would be presented to the oxidizing atmosphere.

Oxidation studies.—Oxidations were carried out in a resistance wire-wound furnace with a static air atmosphere. In most of the experiments, the small panels were placed directly on a nichrome hook which was attached to a pedestal in the hot zone. Thus, it was only required to bring the thin metal strip itself up to temperature. Oxidized samples were cooled in a desiccator before weighing. Hand polished samples blistered upon oxidation for times longer than a few minutes. These samples were weighed, oxidized, and transferred in crucibles.

Oxidation tests, with samples of the four surface preparations described above, were made at 600°, 700°, 800°, and 900°C for various time intervals up to 60 min. The temperature was controlled to ±2°C. Duplicate determinations were made, and, if the precision was poor, further checks.

Chemical analyses.—Oxide layers developed on the alloy by the various treatments were stripped from the metal substrate. The method used involved preferential solution of the metal in a bromine-methyl acetate solvent. This solvent (6 ml bromine in 30 ml methyl acetate) has been used for the isolation of inclusions in various ferrous alloys (4). Residues were filtered off, washed with methyl acetate, dried, and weighed. These were dissolved in 6*N* H_2SO_4 or 6*N* HCl.

The composition of the resultant solutions was determined spectrophotometrically, the nickel in the form of the dimethyl glyoxime complex and the iron as the orthophenanthroline complex. For each analysis the scale was removed and weighed, the iron and nickel separately determined, and the percentage of nickel of total metal analyzed calculated.

Electron diffraction examination of films.—Electron diffraction analyses by the reflection technique were made with a General Electric electron diffraction instrument. An accelerating voltage of 45kv and a filament current of 30–40 μa was used. The exposure varied, being of a duration of as high as 30 sec for certain samples. At least four patterns were obtained for each sample.

Metallographic examination of films.—Several representative oxidized metal strips were examined metallographically by standard techniques. For mounting several samples a resin (Selectron 5003, manufactured by the Pittsburgh Plate Glass Company) which polymerized at low temperature—about 45°C—was employed to preserve the fragile film. In addition, a few samples were studied by the taper section technique (5) which allows the interface to be magnified by a factor of 10X the normal magnification.

Treatment of data.—Examination of oxidation data indicated that the reaction could be represented mathematically by a parabolic equation as

$$(\Delta m)^2 = b + k_p t \qquad \text{(I)}$$

where, m = the gain in weight in g/cm² of a sample oxidized for t seconds; k_p is the parabolic rate constant expressed in $g^2cm^{-4}sec^{-1}$; b is a constant (g^2cm^{-4}).

The temperature dependence of the reaction was represented by the Arrhenius-type equation

$$k_p = Ae^{-Q/RT} \qquad \text{(II)}$$

wherein A is a constant (sometimes called the action constant) and Q is another constant (called the activation energy). The activation energy and action constant were determined for each of the four surface preparations and compared with literature values for the oxidation of nickel and iron.

Results

Kinetics of Reaction

Considering the fact that the plot of the data follows the well-known parabolic relation, it is not

TABLE I. *Parameters of parabolic equation expressing kinetic data*

Temp, °C	k_p ($g^2cm^{-4}sec^{-1}$) ($\times 10^{12}$)	b (g^2cm^{-4}) $\times 10^4$
"As-rolled" surface		
600	1.30	0.00
700	14.7	0.00
800	113	0.00
900	870	0.00
"Sand-blasted" surface		
600	20.7	0.0115
700	135	0.044
800	603	0.110
900	2430	0.040
"Polished" surface		
600	22.5	0.010
700	148	0.025
800	361	0.13
900	933	0.16
"Chemically-cleaned" surface		
600	0.95	0.00032
700	7.90	0.0038
800	45.3	0.030
900	367	0.00

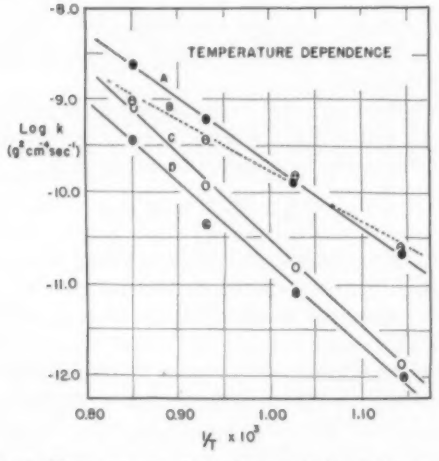

FIG. 1. Temperature dependence of the oxidation rate of the 42% nickel-iron alloy. A = sand-blasted surface; B = polished surface; C = as-rolled surface; D = chemically cleaned surface.

necessary to give these graphs. The equations may be constructed if the values of k_p and b are known. These are given in Table I.

The temperature dependence of the reaction may be concisely shown if log k_p is plotted against $1/T$. This plot is made in Fig. 1. From this the constants in equation (II) were calculated and are given in Table II.

The value of k_p may be taken as a quantitative measure of the oxidation rate. As evidenced in Table I, the oxidation rate of the iron-nickel alloy varies considerably in a manner difficult to explain by the expected surface area relationships. The "chemically cleaned" sample has the lowest rate. Ratios of the other rates to that of the rate of the "chemically cleaned" surface taken as unity are:

Chemically cleaned	As-rolled	Sand-blasted	Polished
1	2	7–22	2.5–24

The as-rolled surface oxidizes at a rate about double that of the chemically cleaned surface and this is fairly consistent varying from 1.4 to 2.5 over the temperature range investigated. However, from a surface area relationship, one would expect the opposite to hold because it is known that an etched surface has a much greater surface area than a rolled surface. Electron diffraction examination revealed that the as-rolled, bright, annealed surface, after exposure to laboratory air, was oxidized, yielding Fe_2O_3 as a reaction product. There was also a small amount of Fe in the surface which may, in itself, account for the greater rate. The sand-blasted surface oxidized at a much greater rate than the chemically cleaned surface, but the ratios between the two rates varied with temperature. At 600°C the ratio of rates was 22 to 1, while at 900°C it was 7 to 1. The increase in surface area may only account for part of this increase, for on this basis, one would expect the factor to remain about the same over the whole temperature range. Some of the sand used in abrading the steel, while not found by the electron diffraction examination of the surface prior to oxidation, was found in the oxide films by chemical analysis. It appears likely that the reason that the factor dropped with temperature may well be explained by the final disposition of the abrasive material. Oxidation measurements made with polished surfaces lacked precision. At 600° and 700° the rates were similar to those obtained with the sand-blasted surface, but at 800° and 900° the rates are considerably lower.

Because of the erratic nature of the results obtained with polished surfaces, the A and Q values in

TABLE II. *Temperature dependence of reaction*

Surface	A (action constant) (g^2cm^{-4} sec^{-1})	Q (activation energy) (cal/gmole)
"As-rolled"	0.129	44,200
"Sand-blasted"	0.00276	32,600
"Polished"	7.0×10^{-5}(?)	25,300(?)
"Chemically cleaned"	0.0124	40,800
Iron	0.37	33,000 (6)
Nickel	0.013–0.151	41,200–46,500(7, 8)

the temperature dependence equation for the reaction are reported as questionable in Table II.

From these results, it is very clear that not only time and temperature but also surface preparation must be exactly prescribed if one is to get a reproducible oxide layer.

Chemical Analyses

Representative results of chemical analyses made on oxide films stripped from samples which were oxidized after chemical cleaning are given as follows.

Oxidation temp, °C	Time, min	Weight gain, mg/cm²	% Ni
600	5.0	0.0465	31.2
800	1.0	0.112	31.8
800	10.0	0.392	17.1

The per cent Ni reported is from a total weight of iron plus nickel found in the film. It is apparent that the first formed film is rich in nickel.

Further stripping and analyses were made with samples that had been sand-blasted before oxidation.

Oxidation temp, °C	Time, min	Weight gain, mg/cm²	% Ni
800	0.5	0.209	13.3
700	10	0.392	6.3
800	30	1.05	5.6

These three tests were taken as representative of 15 analyses. Here, too, there is a greater percentage of nickel in the thin films. The nickel content decreases as the film grows and reaches a fairly constant value of 5–6% of the metal content in the film. However, the gradation is considerably less marked than in the films developed on chemically cleaned alloys. Considering that the 5–6% represents an average value for the film which is high in nickel near the metal-oxide interface, it is evident that nickel is either present in low concentration or absent from these layers removed from the interface. Strippings were carried out in a quantitative manner and it was observed that there was present a fair amount of acid-insoluble material, identified as the sand (quartz) with which the samples had been abraded. This sand has been embedded in the metal, but was so located beneath the surface that it had not been observed in the preliminary electron diffraction examination of these sand-blasted samples.

Electron Diffraction Analyses

In considering the results of the electron diffraction experiments, certain observations should be borne in mind. The formation of nickel ferrite ($NiFe_2O_4$) or iron ferrite (Fe_3O_4) seems possible. These ferrites crystallize in the spinel (face-centered cubic) form and have similar lattice constants, i.e., $NiFe_2O_4$ has an $a = 8.34$ and Fe_3O_4 an $a = 8.37$. The electron diffraction reflection method of determining lattice constants is not sufficiently accurate to differentiate between these two structures although, as discussed below, one may speculate on the existence of one structure or the other if several lines of evidence are available. Below, the term "ferrite" includes both structures.

TABLE III. *Electron diffraction analyses of oxide films, surfaces chemically cleaned before oxidation*

Temperature oxidized, °C	Time oxidized, min	Weight gained during oxidation, mg/cm²	Patterns found
600	3	0.0078	Fe_2O_3, ferrite
600	5	0.0194	Fe_2O_3, ferrite
600	40	0.284	Fe_2O_3, ferrite, Ni(?)
700	7	0.0621	Fe_2O_3, NiO, Ni
700	30	0.135	Fe_2O_3, ferrite, Ni
700	1	0.0078	Fe_2O_3, ferrite
800	0.5	0.0155	Fe_2O_3, ferrite
800	3	0.135	Fe_2O_3, ferrite, Ni

TABLE IV. *Electron diffraction analyses of oxide films, surfaces sand blasted before oxidation*

Temperature oxidized, °C	Time oxidized, min	Weight gained during oxidation, mg/cm²	Patterns found
600	20	0.213	Fe_2O_3, Fe, NiO
700	2.5	0.209	Fe_2O_3, ferrite
700	10.0	0.392	Fe_2O_3, ferrite, Fe, Ni
700	60	0.695	Fe_2O_3, ferrite, quartz
800	0.5	0.213	Fe_2O_3, ferrite, quartz
800	20	0.913	Fe_2O_3, ferrite, quartz
800	30	1.19	Fe_2O_3, ferrite, quartz
900	40	2.49	Fe_2O_3, ferrite, quartz

In the following descriptions the constituent reported first was present with certainty. Other constituents for which there was evidence are also reported. The depth of penetration of the electron beam (200–300 Å) is such that, in a thick oxide layer of duplex structure, the outer layer would give the most pronounced pattern even though it might well be present in lesser amount. The first series analyzed reported in Table III had been chemically cleaned before oxidation. A second series was run with samples that had been sand-blasted prior to oxidation. The observations are reported in Table IV.

The main products of oxidation, viewed after the samples cooled to room temperature, were Fe_2O_3 and ferrite. In the thin films on the chemically cleaned samples these were the only compounds found. However, Ni was found when the films had increased in thickness. The sand-blasting technique used in preparing the second series of samples allowed quartz to be found in the films. Generally speaking, the products were Fe_2O_3 and ferrite.

A further sample was taken as-rolled and oxidized:

Oxidation temp, °C	Oxidation time, min	Weight gained, mg/cm²	Patterns
700	40	0.194	Ferrite, Fe_2O_3 (both distorted)

From the electron diffraction study, it may be concluded that alpha-Fe_2O_3 and a ferrite are consistently obtained upon oxidation of this alloy.

Metallographic examination of films.—The microscopic examination of the oxidized alloy strips (Fig. 2 and 3) demonstrate that two phases are present in stratified layers. The layer closest to the alloy is identified as the ferrite, while the lighter phase further removed from the alloy is alpha-Fe_2O_3. The taper section mount made of an oxidized sand-blasted surface accentuates the two-phase character of the film. This high magnification gives ample evidence of the high probability of entrapping metal in stripping the oxide film.

Some internal oxidation was seen in all of the metallographic sections at high magnification. However, the amount was not believed to be an important factor in the kinetics. The photomicrographs exhibited are of sand-blasted surfaces. The other surfaces appeared to oxidize in a manner that gave slightly more uniform layers but there was no qualitative difference in the oxide layers formed. In the very thin films the major portion of the oxide was ferrite. When cracking occurred within the film,

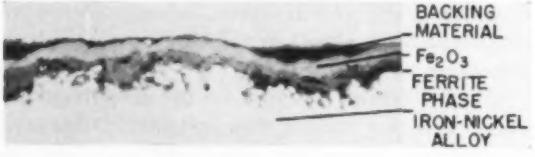

FIG. 2. Oxide film on iron-nickel alloy prepared by sand blasting. Oxidized for 60 min at 700°C. 2000× before reduction for publication.

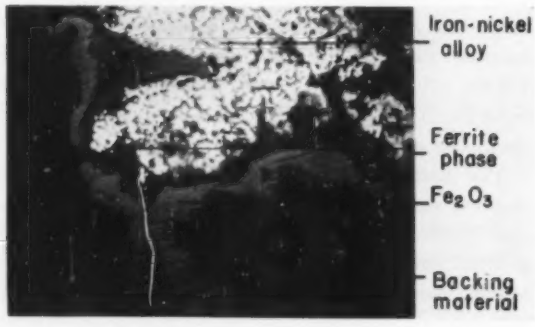

FIG. 3. Oxide film on iron-nickel alloy prepared by sand blasting. Oxidized for 60 min at 700°C. Magnification in vertical direction, 15,000×, in horizontal direction, 1500×, before reduction for publication.

it did so in the ferrite phase indicating that that phase was in a stressed condition.

DISCUSSION

Electron diffraction analyses of these films made after cooling from the reaction temperature yielded evidence for both a ferrite and Fe_2O_3. Thermodynamically, Fe_2O_3 is stable at these temperatures (9). Gulbransen and Hickman (10) found that, as the oxide film which was grown on iron increased in thickness, the compound alpha-Fe_2O_3 was stable at higher and higher temperatures.

It is postulated that the ferrite is $NiFe_2O_4$ rather than Fe_3O_4. Ni in high concentration was found by chemical analyses of the stripped film. Also, calculation from many samples indicates a lattice constant a = 8.33 Å. Although literature values for $NiFe_2O_4$ are 8.34 Å and for Fe_3O_4, 8.37–8.40 Å, Hickman and Gulbransen (3) report 8.42–8.43 Å for Fe_3O_4 when this compound is grown on an iron surface during oxidation. The a value from the authors' experiments agrees well with that reported by Koh and Caugherty (8.36 Å) but not with that of Hickman and Gulbransen (8.43 Å). There is no obvious explanation for these different structures other than the limited accuracy of the experimental technique.

The rate-controlling factor in this reaction is diffusion through this nickel ferrite layer. In cases where the reaction rate is low, a high concentration of nickel was found in the film next to the basis metal. Diffusion rates in spinels have been observed to be lower than in the parent oxide (11). Also, Quarrell has indicated that spinels stabilized with Ni or Cr are more protective than Fe_3O_4 (12). The existence of a continuous series of spinels with gradations of nickel content is in accord with what is known of the chemical composition of these compounds as Ni^{++} or Fe^{++} can exist in substitutional solid solution in a spinel whose nominal formula is $NiO \cdot Fe_2O_3$.

The sand-blasting preparation appears to hinder formation of a ferrite as rich in nickel as that formed on the chemically clean surface. The early nucleation of $NiFe_2O_4$ may be adversely influenced by the distorted structure, the presence of Fe_2O_3, or the presence of the quartz.

Results with a polished surface were lacking in precision. The calculated activation energy is not believed to be significant, insofar as a particular mechanism is concerned. Rather, it appears that at low temperatures a mechanism similar to that of the sand-blasted surface appears to be followed while at higher temperature that of the as-rolled surface.

Thus, it may be concluded that the method of surface preparation influences the composition of

the oxide formed and consequently has a major bearing on the rate of oxidation. Quarrell observed that either Fe_2O_3 or Fe_3O_4 could be formed by heating iron at 400°C depending on the type of abrasive (13). The favoring of the nucleation and growth of one oxide over another appears to be parallel with the case described here.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

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High Temperature Corrosion Rates of Several Metals with Nitric Oxide[1]

MILTON FARBER,[2] ALFRED J. DARNELL,[3] AND DONALD M. EHRENBERG

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

ABSTRACT

An experimental study has been made of the high temperature corrosion rates of various metal filaments with nitric oxide. Corrosion rates have been determined for iron, tantalum, tungsten, molybdenum, nickel, copper, silver, and the alloys Inconel,[4] and stainless steel. The temperature range included temperatures from 800° to 2000°K. The metals in order of decreasing corrosion resistance are Inconel, 25–20 stainless steel, molybdenum, nickel, tantalum, 18–8 stainless steel, tungsten, iron, and copper.

INTRODUCTION

Concerning reactions of metals with NO, some previous work of a qualitative nature has been reported. Adhikary (1) found that gold, silver, and iron were oxidized at temperatures above 650°K when NO and H_2 were passed over the heated metal. The NO was reduced to NH_3. Schröder and Tamman (2) studied the reactions of NO on various metals over a wide range of pressures and temperatures. They measured the thickness of the oxide coating on metal foils and found that the oxidation of copper with NO began at temperatures above 100°C. Also, they found that the corrosion rate was similar to that of Cu and O_2; however, upon increasing the pressure the reaction rate began to decrease. Reaction rates of iron in NO at temperatures of 600° to 700°K were observed by Schröder and Tamman to be similar to those of Fe and O_2. They found that, when Ni was subjected to NO at temperatures from 800°–1000°K, initially an impermeable film was formed which later became porous, and the reaction rate was accelerated. DeVoogd and Tadema (3) studied the resistance of different metals in flue gases containing NO.

Wise and Frech (4) made a study of the decomposition of NO in a quartz vessel over a wide temperature range. They obtained two expressions for the specific reaction-rate constant for this process. At temperatures above 1500°K a homogeneous mechanism prevails which has an activation energy of 78.2 kcal, whereas below 1000°K a heterogeneous mechanism applies which has an activation energy of 21.4 kcal. At temperatures between 1000° and 1500°K both heterogeneous and homogeneous mechanisms contribute to the decomposition rate of NO. It is interesting to note that, since the corrosion mechanism is heterogeneous, it would be expected that only the lower activation energy would be significant. This lower value is consistent with the observation that in all but one reaction (*see* Ta-NO under Results) the observed activation energies were less than 78 kcal/mole.

In studying the reaction of a metal with NO it is necessary to consider the surface of the metal and its temperature and to know whether the gas is reacting in its pure state or in a decomposed form. The gas-metal reaction involved is the formation of an oxide, nitride, or both.

$$XM + Y/2O_2 = M_XO_Y$$

$$XM + Y/2N_2 = M_XN_Y$$

Heat liberated upon the formation of the metal oxides from the elements varies from 7 kcal/mole for Ag_2O to 500 kcal/mole for Ta_2O_5. Thus, a consideration of the heat of formation of the metal oxide (or nitride) with thermal data for decomposition may aid in interpreting a particular mechanism.

EXPERIMENTAL PROCEDURE

The authors have previously employed this method for measuring the corrosion rates of various metals with H_2S and SO_2 (5) and only a brief description of the apparatus will be given here. Garner, Gray, and Stone (6) studied the reaction rate of copper with oxygen by measuring the increase in resistance of a copper film which was plated on the walls of a glass bulb. Wilson (7) and Hudson (8) studied corrosion rates by measuring the change in electrical conductivity of flat metal strips. The

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[2] Present address: Aerojet-General Corporation, Azusa, California.

[3] Present address: General Petroleum Corporation, Los Angeles, California.

[4] Inconel is registered trade mark of the International Nickel Company.

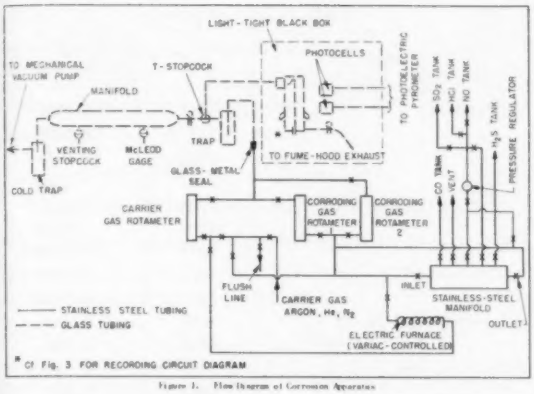

FIG. 1. Flow diagram of corrosion apparatus

method employed here and described in detail earlier (5) is concerned with the measurement of the change in resistance of a metal filament (hot wire) of 0.010 in. diameter in a corrosive medium. Since the corrosion rate is obtained directly from the resistance change, a recording mechanism is necessary to indicate the current and voltage across the filaments. Fig. 1 describes the arrangement of the equipment used to conduct corrosion rate experiments.

An exhaust manifold connected directly to a vacuum pump is used to evacuate the reaction bulb which is mounted in a light-tight box. The vacuum is measured by means of a McLeod gauge. The bulb is filled to atmospheric pressure with an inert carrier gas from the gas manifold, shown in Fig. 1, to which steady flow rates (as measured with rotameters) are maintained by use of a series of needle valves before and after the flowmeters. These rates are of the order of 100 cc/min of gas. The incoming inert gas (argon or N_2) is passed through an electrically heated tube filled with copper turnings to remove traces of oxygen impurities that may be present in the commercially purchased gas cylinders. After the bulb has been filled to atmospheric pressure, the filament is heated electrically to the desired temperature. The temperature is maintained by adjusting the resistance controls with the aid of either a photoelectric or an optical pyrometer, calibrated with the use of standard resistance data for tungsten filaments. The operation of the photoelectric pyrometer and the equations involved were given in detail earlier (5).

The corroding gas is metered through a separate rotameter into a manifold (from 1–10% of the total gas), together with the carrier, where mixing occurs for a period varying from 30 to 100 sec before the mixture enters the bulb. As the reaction takes place, the current and voltage are recorded simultaneously. Temperature is maintained by holding the response ratio of the two photocells constant or by means of an optical pyrometer. The duration of most runs was 220 or 240 sec. All plots of A/A^o vs. time (sec) were nearly linear (not shown), and the values of k in Table I are the slopes of these lines.

In order to obtain uniform corrosion of the wire, it is necessary to use filaments which have been accurately machine-drawn. Thus, hot spots can be eliminated, and consistent burnout times obtained, justifying the resistance method for measuring corrosion rates.

THEORY

The corrosion rate is directly proportional to the resistance change since resistance R is a function of the length and diameter of the filament

$$R = \rho l/A$$

where ρ = resistivity of wire, l = length of wire, and A = cross-sectional area of wire.

Since the specific resistivity ρ is a function of temperature only, for a constant length filament the rate of change of resistance with time at constant temperature is proportional to the rate of change of area. If R_o is the initial resistance and R is the resistance after time t, then

$$R_o/R = A/A_o$$

or

$$\frac{R - R_o}{R} = \frac{A_o - A}{A_o}$$

which leads to

$$\Delta R/R = -\Delta A/A_o$$

Three different rate laws have been proposed for corrosion processes: the parabolic rate law of Pilling and Bedworth (9) and the rectilinear and logarithmic rate laws (10, 11). For a cylindrical wire of initial cross-sectional area A_o and radius r_o, the thickness of the film dy for initial corrosion would be proportional to the decrease in radius r of the wire with time t, as shown in Fig. 2.

In order to obtain an expression for the parabolic rate law for cylindrical wires it is necessary to set up the rate law in differential form for the wire. For an initial radius of r_o the parabolic rate law in differential form is

$$-dr/dt = k/(r_o - r)$$

which integrates to

$$r^2 - 2r_o r + r_o^2 = 2kt$$

and in terms of the cross-sectional area becomes

$$A/A_o = 1 - 2\sqrt{\frac{2\pi kt}{A_o} + \frac{2\pi kt}{A_o}}$$

(parabolic rate law)

TABLE I. *Initial corrosion rates for several metals with nitric oxide*

Gas mixture: 95% Argon and 5% NO

Metal	T (°K)	k (% area loss/sec)
Iron	970	0.0165
	1040	0.0215
	1100	0.0270
	1154	0.0345
	1167	0.0390
	1176	0.0420
	1187	0.0440
	1204	0.0505
Tantalum	1468	0.0065
	1500	0.0125
	1516	0.0110
	1532	0.0305
	1637	0.0485
	1730	0.0760
Tungsten	1381	0.010
	1431	0.020
	1454	0.037
	1525	0.070
	1548	0.096
	1602	0.085
	1636	0.110
	1676	0.100
	1767	0.120
	1825	0.170
	1893	0.170
Molybdenum	1429	0.0036
	1445	0.0076
	1455	0.0031
	1467	0.0075
	1493	0.0086
	1571	0.0306
	1584	0.0214
	1637	0.0347
	1699	0.0443
	1723	0.0461
	1774	0.0880
	1808	0.132
	1842	0.132
Nickel	1093	0.00134
	1104	0.00267
	1123	0.00467
	1154	0.00800
	1189	0.0153
	1212	0.0107
	1239	0.0260
	1255	0.0167
	1288	0.0260
	1297	0.0180
	1308	0.0305
	1333	0.0387
	1355	0.0120
	1383	0.0153
	1415	0.0153
	1464	0.0093
	1474	0.0073
	1520	0.0147
	1536	0.0067
	1593	0.0060
	1649	0.0053
	1651	0.0060
Copper	1113	0.0250
	1113	0.0255
	1160	0.0300
	1167	0.0280
	1208	0.0340
	1209	0.0370
	1247	0.0380
	1251	0.0400
	1271	0.0430
Stainless steel 25–20	1538	0.001
	1558	0.002
Stainless steel 18–8	1453	0.016
	1503	0.023

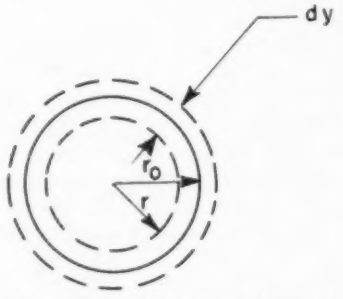

FIG. 2. Cross-sectional diagram of corrosion film on a wire.

Since the formation of oxide film is directly related to the loss in diameter of a cylindrical wire, the rectilinear rate law can be expressed in terms of diminishing radius as

$$-dr/dt = k$$

which integrates to

$$r_o - r = kt$$

and in terms of cross-sectional area becomes

$$A/A_o = 1 - 2(\pi/A_o)^{\frac{1}{2}}\, kt + \pi/A_o\, k^2t^2$$

(rectilinear rate law)

The equation for the logarithmic rate law can be expressed for cylindrical wires as

$$-dr/dt = ke^{-(r_o - r)}$$

which upon integrating and expressing in logarithmic form yields

$$(r_o - r) = \ln(1 + kt)$$

This expression in terms of the cross-sectional area becomes

$$A/A_o = 1 - 2(\pi/A_o)^{\frac{1}{2}} \ln(1 + kt) + \pi/A_o \ln(1 + kt)^2$$

(logarithmic rate law)

The logarithmic rate law can be simplified for

initial thin coatings. The values for k are small (less than 0.01 in most cases) and for small values of t the third term can be neglected and the expression simplified to

$$A/A_o \cong 1 - 2(\pi/A_o)^{\frac{1}{2}}\, kt$$

(logarithmic rate law for thin coatings)

The results obtained for the metals studied (*see* Results) show that the initial rate of corrosion was nearly always linear with time as

$$-dA/A_o = k/100\, dt$$

where k is expressed as per cent area change per second. This expression in integrated form is

$$A/A_o = 1 - k/100\, t$$

(experimental rate law)

This expression is similar to the logarithmic rate law for thin coatings and also to rectilinear rate law for initial corrosion, wherein the third term is small compared to the second.

If the logarithm of the reaction rate is plotted against the reciprocal of the absolute temperature, an equation of the Arrhenius-type generally occurs, which when expressed in logarithmic form is

$$\ln \text{ rate} = \ln a - E/RT$$

where E is the activation energy for the over-all process and a is the frequency factor. Both a and E are usually constant over a small temperature range. From this, it can be seen that a plot of ln rate vs. $1/T$ yields a straight line.

During the corrosion period a film is formed on the surface of the pure metal. The conductivity of the oxide coating is negligible compared with that of the pure metal. Veil (12) measured the resistivity of various oxides at high temperatures. He found for CuO at 1000°C a resistivity of 3×10^{-1} ohm cm which compares to the resistivity of Cu of 9×10^{-6} ohm cm at 1000°C. The resistivity of Fe_2O_3 at 1000°C was found to be 82 ohm cm as compared to 50×10^{-6} ohm cm. The resistivity of NiO at 1000°C is 144 ohm cm which compares to 62×10^{-6} ohm cm at 1000°C for pure Ni. The above examples show that conductivities of metal oxides are negligible to those of the pure metals.

The effect of the solubility of the gases on the resistance of the metal filaments investigated was negligible since there was no discernible change in their resistance at temperatures just below the point of corrosion. However, it was not possible to study the corrosion rates of metals such as zirconium or titanium because the solubility of oxygen and nitrogen changed their resistivities to such an extent that the change in resistance due to corrosion could not be measured.

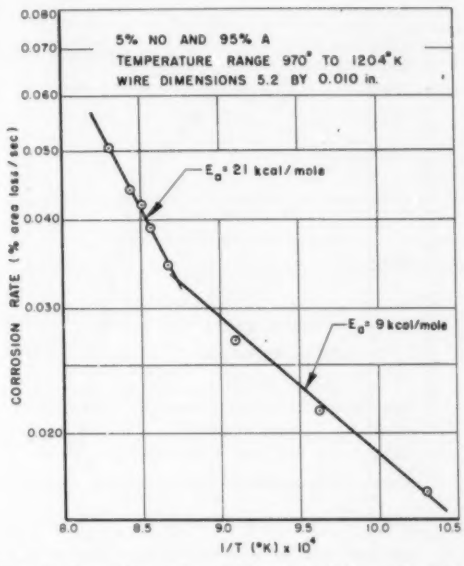

FIG. 3. Corrosion rate of Fe with NO as function of $1/T$.

RESULTS

Corrosion rates of iron with NO.—Corrosion rates of iron in an atmosphere of NO (5%) and A (95%) and at a constant gas flow rate of 100 cc/min were studied over a temperature range of 970° to 1200°K. The iron employed was Armco[5] iron of better than 99% purity.

Corrosion of iron in nitric oxide is quite rapid at all temperatures. Rate constants vary from 0.016 to 0.050 (% area loss/sec) over the range studied (cf. Table I). The temperature dependence of the rate tends to increase at temperatures over 1100°K. When the logarithm of the rate constant is plotted against the reciprocal of the absolute temperature, two activation energies are obtained over the temperature range studied, namely 9 kcal/mole from 970° to 1140°K and 21 kcal/mole from 1140° to 1200°K (cf. Fig. 3). The scale formed consisted entirely of various oxides of iron.

Corrosion rates of tantalum with NO.—Tantalum is much more resistant to corrosion with NO than is iron and shows very little corrosion in the low temperature range. The reaction rate at temperatures below 1400°K could not be detected. Therefore, it was necessary to obtain corrosion rate data in the range from 1450° to 1730°K. The increase in reaction rate with temperature was very rapid between 1470° and 1550°K.

Corrosion of tantalum with NO, together with that of several of the other metals including iron, gives two curves of apparent activation energy over

[5] Armco is registered trade mark of American Rolling Mill Company.

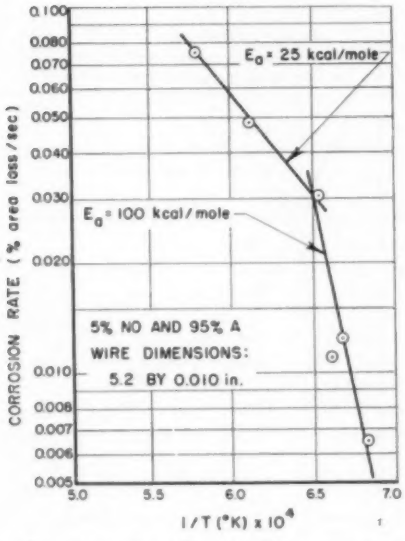

FIG. 4. Corrosion rate of Ta with NO as function of $1/T$

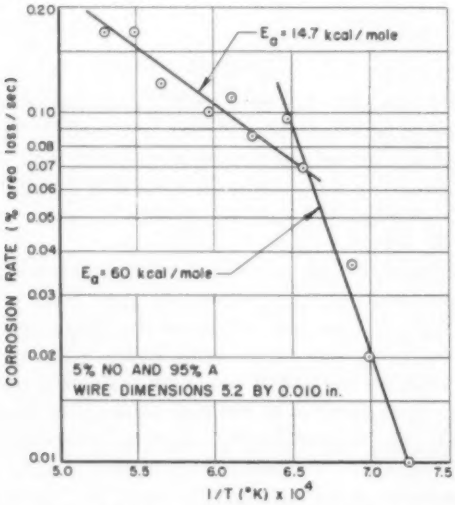

FIG. 5. Corrosion rate of W with NO as function of $1/T$

the temperature range studied. In the lower temperature region (cf. Fig. 4) an activation energy of 100 kcal/mole is obtained, whereas the higher range gives an activation energy of 25 kcal/mole. Rate constants vary from 0.006 (% area loss/sec) at 1470°K to 0.076 at 1730°K (cf. Table I).

Corrosion rates of tungsten with NO.—The reaction rate of W with NO depends mainly on the availability of molecular or atomic oxygen from the decomposition of NO. In order to ascertain the dependence of oxygen concentration on the corrosion rates of W, an experimental study was made with both NO and O_2. In both cases the gas mixture contained 95% A as the inert gas and 5% of either O_2 or NO as the corroding gas.

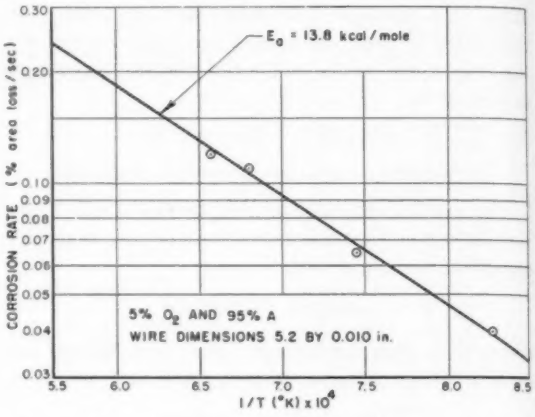

FIG. 6. Corrosion rate of W with O_2 as function of $1/T$

TABLE II. *Initial corrosion rates of tungsten and molybdenum with oxygen*

Gas mixture: 95% Argon and 5% oxygen

Metal	T (°K)	k (% area loss/sec)
Tungsten	1209	0.040
	1343	0.065
	1468	0.110
	1522	0.120
Molybdenum	1209	0.046
	1333	0.062
	1406	0.101
	1506	0.138
	1605	0.145

Corrosion rates of W with NO were taken over a temperature range of 1380° to 1890°K, and the rates with O_2 over the temperature range of 1200° to 1520°K. As can be seen from Fig. 5, the NO corrosion rates vary greatly with temperature in the region from 1300° to 1400°K, namely, from 0.01 to 0.07 (% area loss/sec). Corrosion rates increase rather slowly with temperature from 1400° to 1750°K, namely, from 0.07 to 0.18 (% area loss/sec).

A higher corrosion rate would be expected with O_2 since, as postulated, the rate of corrosion of W depends upon the dissociation of NO for availability of O_2. The corrosion rate of W with O_2 increases uniformly with temperature from 0.04 (% area loss/sec) at 1150°K to 0.12 at 1525°K.

The apparent activation energies as obtained from Fig. 6 are 13.8 kcal/mole for O_2 as compared to 14.7 kcal/mole for NO (cf. Fig. 5) at the higher temperatures. The fact that these energies are nearly equal indicates that the rate of dissociation of NO in this temperature range is not rate-determining in the corrosion process. In the low temperature range the apparent activation energy for NO is 55 kcal/mole. The rate constants for the reaction

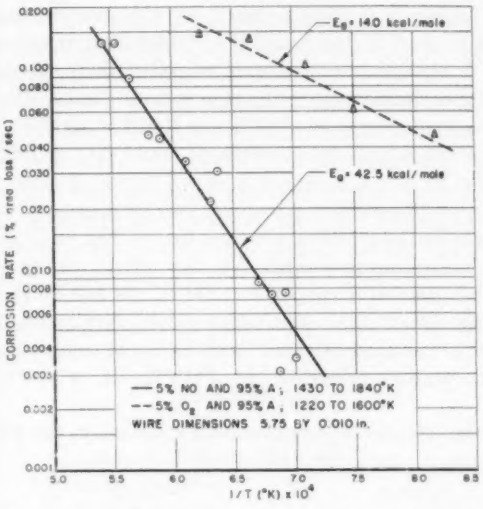
E_a = 14.0 kcal/mole
E_a = 42.5 kcal/mole
CORROSION RATE (% area loss/sec)
1/T (°K) x 10⁴
— 5% NO AND 95% A; 1430 TO 1840°K
-- 5% O₂ AND 95% A; 1220 TO 1600°K
WIRE DIMENSIONS 5.75 BY 0.010 in.

FIG. 7. Corrosion rate of Mo in NO and O_2 atmosphere as function of $1/T$.

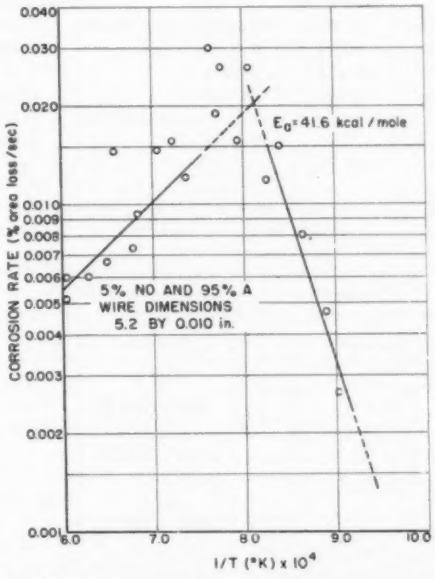

FIG. 8. Corrosion rate of Ni with NO as function of $1/T$

rates of W and NO and O_2 are given in Tables I and II, respectively.

Corrosion rates of molybdenum with NO.—Molybdenum is quite resistant to corrosion in NO at temperatures below 1400°K but reacts quite readily at higher temperatures. Corrosion rates for Mo were obtained over a temperature range of 1400° to 1850°K. Rate constants (cf. Table I) vary from 0.0036 to 0.132 (% area loss/sec) over the temperature range studied, the activation energy being 43 kcal/mole as shown in Fig. 7. As in the case of tungsten, reaction rates of Mo were obtained with both O_2 and NO; corrosion of Mo with O_2 (95% A-5% O_2) was more rapid for a given temperature than was the rate with NO. An apparent activation energy shown in Fig. 7 gives a value of 14.0 kcal/mole for O_2 over the temperature range of 1220° to 1600°K. Gulbransen and Wysong (13) have obtained an activation energy of 36.5 kcal/mole for Mo in 7.6 cm of O_2 over a lower temperature range of 620° to 820°K.

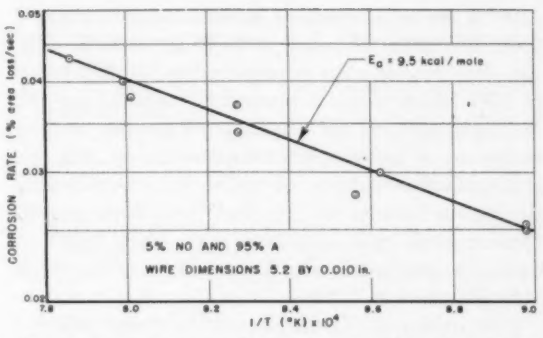

FIG. 9. Corrosion rate of Cu with NO as function of $1/T$

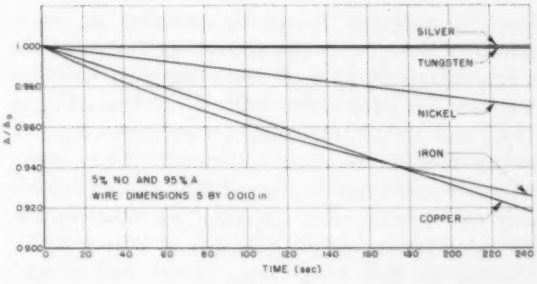

FIG. 10. Corrosion rates of several metals with NO at 1200°K.

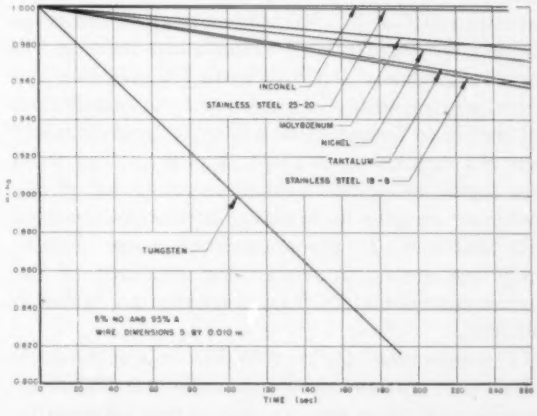

FIG. 11. Corrosion rates of several metals with NO at 1450°K.

Corrosion rates of nickel with NO.—Reaction rates of Ni with NO were studied over the temperature range of 1100° to 1650°K. Rates increase steadily until a temperature of 1200°K is attained. Above

1200°K the rate starts to decrease from a peak of 0.025 (% area loss/sec) to 0.005 at 1650°K. The rate-determining step is presumably the formation of NiO which forms a protective coating over the Ni. Upon plotting the logarithm of the rate vs. the reciprocal of the absolute temperature (cf. Fig. 8), a considerable amount of scatter was obtained in the region because of the oxide transition region. Experimental rate constants vary from 0.002 to 0.030 (% area loss/sec) and are listed as functions of temperature in Table I.

Two oxides of Ni are known to exist, namely, Ni_2O_3 and NiO. Since at high temperatures the Ni_2O_3 decomposes to the lower oxide, it was believed that the corrosion rate could probably be determined by the type of oxide formation. Consequently, x-ray diffraction patterns were taken in both the high and low temperature regions. Oxide samples at 1100° and 1570°K (at which temperatures the corrosion rates are the same) were analyzed for crystal structure and type of oxide. Both samples showed only one type of oxide, namely, NiO; however, the low temperature sample consisted of large crystals, whereas the high temperature sample had a small and compact crystalline structure.

Corrosion rates of copper with NO.—Reaction rates of Cu with NO were measured in an NO gas mixture (95% A–5% NO) over a temperature range from 1100° to 1275°K. A uniform rate increase was obtained, namely, 0.025 to 0.043 (% area loss/sec) over the temperature range studied. An examination of the oxide formed showed it to be predominantly the red cuprous oxide Cu_2O. A plot (cf. Fig. 9) of the logarithm of rate against the reciprocal of the temperature gave an apparent activation energy of 9.5 kcal/mole. In the temperature range studied, only one activation energy and one form of the oxide were obtained. Rate constants are given in Table I.

Corrosion rates of silver with NO.—Since the oxide of silver is unstable at temperatures over 500°K, no corrosion of silver was expected in the temperature range studied, 900°–1100°K. This fact was verified experimentally.

Corrosion rates of Inconel and stainless steel with NO.—Because of the considerable application of various alloys at high temperatures, it was considered of interest to obtain the reaction rates of Inconel and both 18-8 and 25-20 stainless steel with NO.

At all temperatures below the melting point the corrosion rate of Inconel with NO was negligible, and no temperature-time curves could be obtained. Stainless steel 25-20 (25% chromium-20% nickel) was nearly as resistant as Inconel, corroding only slightly at 1550°K and above. The rate constant (cf. Table I) at 1538°K was 0.001 (% area loss/sec) and at 1558°K had doubled to 0.002. Stainless steel (18% chromium-8% nickel) corroded more readily at these temperatures, the rate constant being 0.016 (% area loss/sec) at 1450°K and 0.023 at 1500°K.

Corrosion rates of several metals with NO *at 1200° and 1450°K.*—A comparison of the corrosion rates of the several metals was made at two temperatures by obtaining the temperature-time curves. Fig. 10 shows the corrosion rate with NO for silver, tungsten, nickel, iron, and copper at 1200°K. As can be seen in the figure, silver and tungsten are very resistant at this low temperature. Both iron and copper are quite readily corroded. At 1450°K (cf. Fig. 11),

TABLE III. *Initial corrosion rates of several metals with* NO *at 1200° and 1450°K*

At 1200°K		At 1450°K	
Metal	k (% area loss/sec)	Metal	k (% area loss/sec)
Silver	Negligible	Inconel	Negligible
Tungsten	0.0005	Stainless steel 25–20	0.001
Nickel	0.013	Molybdenum	0.009
Iron	0.034	Nickel	0.011
Copper	0.039	Tantalum	0.015
		Stainless steel 18–8	0.017
		Tungsten	0.097

TABLE IV. *Activation energies for the reaction of several metals with* O_2 *and* NO[a]
Gas (pressure = 1 atm)

Metal	5% O_2–95% A		5% NO–95% A	
	E (kcal/mole)	a	E (kcal/mole)	a
Fe	—	—	9.0 (950°–1150°K)	1.79
	—	—	21.0 (1150°–1225°K)	3.40×10^2
Ni	—	—	41.6 (1090°–1220°K)	5.04×10^5
	—	—	—	—
Cu	—	—	9.5 (1100°–1270°K)	1.84
W	13.8 (1200°–1550°K)	12.1	60 (1390°–1510°K)	2.95×10^7
		—	14.7 (1510°–1900°K)	8.85
Mo	14.0 (1220°–1600°K)	13.3	42.5 (1430°–1840°K)	1.5×10^4
Ta	—	—	100 (1470°–1540°K)	4.81×10^{13}
	—	—	25 (1540°–1740°K)	1.09×10^2

[a] E = activation energy; a = exponential constant; $k = ae^{-E/RT}$

however, tungsten is corroded quite readily, whereas the 25-20 stainless steel and Inconel are the most resistant to corrosion.

As is shown in Fig. 10 and 11, the metals in order of decreasing corrosion resistance are Inconel, 25-20 stainless steel, molybdenum, nickel, tantalum, 18-8 stainless steel, tungsten, iron, and copper. Corrosion-rate constants are listed in Table III. The apparent activation energies for the several metals and NO are listed in Table IV.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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Organic Peroxides as Source of Cations[1]

ANDREW GEMANT

Engineering Laboratory and Research Department, The Detroit Edison Company, Detroit, Michigan

ABSTRACT

This is a continuation of a study on the problem of oxidation in service of electrical insulating liquids. Oxidation of such liquids, hydrocarbons by their constitution, is accompanied by increased electrical conductivity. In the present study, ozone was used as an agent for accelerated oxidation. It was found that aromatic hydrocarbons in the presence of small amounts of aliphatic acids on ozonization produce very high conductivities. This finding is significant because both aromatics and aliphatic acids may be present in small concentrations in insulating oils. By a detailed study of the effect observed, using ultraviolet absorption spectroscopy and measurement of paramagnetic susceptibility, among others, an attempt was made to establish the chemical nature of the ions that cause the high electrical conductivity.

PURPOSE OF STUDY

The following observations on oxidation-ions in electrical insulating hydrocarbon liquids have been made (1). Oxidation of aromatic orthodiols produces ions that are probably semiquinone type compounds. Reduction of these ions causes reversion to their original nonionic species. Ultraviolet irradiation of ortho-alkylated aromatics also produces ions. The positive ions are probably oxonium-ions of the aldehydes formed. These ions are also partially reducible to nonionic molecules.

This paper describes observations of high electrical conductivities, hence ion-concentrations, which exceed those reported previously by about three orders of magnitude. The chief source of these ions appears to be aromatic hydrocarbons. Ozone was used as the oxidizing agent since the amount acting on the substrate can be controlled easily.

When ozone oxidizes an aromatic hydrocarbon, the increase in electrical conductivity is negligibly small. The novel observation made in this study was that addition of a small concentration of aliphatic acid prior to oxidation with ozone produces high electrical conductivities of 10^{-9} mho/cm or more.

Whereas the chemical nature of the ions produced cannot be stated with certainty, it is possible on the basis of the various observations to describe their structure in a tentative manner.

BASIC OBSERVATIONS

Ozonization was carried out by bubbling ozone through the solution in a glass container without a catalyst. Ozone was produced in a glass-lined corona ozonizer, through which oxygen was passed. The field in the ozonizer could be varied, thus changing the ozone concentration in the stream. In the majority of experiments the field was about 27 kv_{max}/cm which corresponds to a corona current of about 0.15 ma. The rate of flow of oxygen was 200 cc/min, and the ozone concentration in it was 0.25%.

Of the various hydrocarbons, toluene was found most effective in increasing the conductivity, and it was used in most of the experiments. Myristic acid, generally at 20 mM/l, was used in the majority of experiments. All tests were carried out at room temperature.

Some of the crystalline compounds used in this and in previous studies were recrystallized from best Eastman products. Usually, no noticeable difference in conductivity increases was found between the original and purified compounds.

Fig. 1 shows a typical conductivity effect. After an hour the conductivity, σ, reached a level of about 5×10^{-10} mho/cm. The solution remained clear and had a faint yellow color.

Fig. 2 shows the increase of conductivity with increasing ozonizer field, i.e., ozone concentration.

These high ion concentrations are not permanent, indicating that the ions are probably intermediate oxidation products. Fig. 3 shows the time behavior of conductivity after oxidation. As a rule σ stays on a high level for about two days (a frequent initial increase in the first few hours is not shown), after which it drops rather rapidly. In about six days it reaches either a moderately high, constant level of about 3×10^{-12} (curve 1), or drops even lower (curve 3). In a mixture of toluene and transformer oil (curve 2) a moderately high level was obtained. This may be due to unsaturated compounds in the oil competing with toluene for the ozone.

The instability of σ is an indication that the high conductivity is not caused by a strongly polar decomposition product, for instance, benzaldehyde. Moreover, in such a case the dielectric constant

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should show a marked increase which, however, is not observed. Water, as a possible oxidation product, cannot be the cause of the increased conductivity, since even saturation with water produces only small changes in conductivity. Carbon dioxide, a possible cleavage product of the peroxides, cannot increase the conductivity; in fact, it is sometimes used as a pressure medium in oil-impregnated high voltage cables.

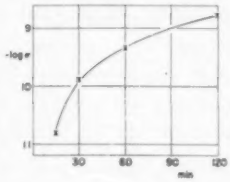


FIG. 1

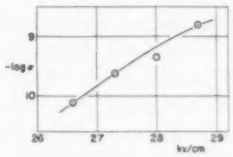


FIG. 2

FIG. 1. Electrical conductivity σ (mho/cm) vs. time of oxidation. Myristic acid (20 mM/l) in toluene. Ozonizer field 27.3 kv/cm.

FIG. 2. Conductivity vs. ozonizer field. 0.020*N* myristic acid in toluene. Oxidation time 60 min.

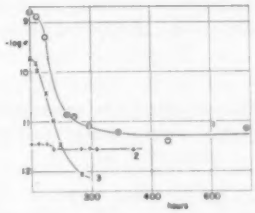


FIG. 3. Conductivity vs. time passed after oxidation. 0.02*N* myristic acid in toluene (curve 1); toluene-transformer oil 1:1 (curve 2); toluene-paraffin oil 1:1 (curve 2).

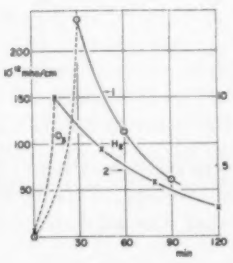


FIG. 4

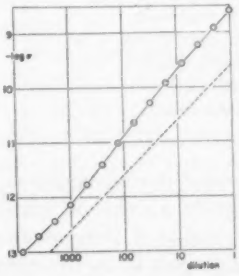


FIG. 5

FIG. 4. Decrease in conductivity on reduction in H_2 stream. 0.01*N* myristic acid in toluene. Oxidation time: 30 min for curve 1 (left-hand side ordinates), 15 min for curve 2 (right-hand side ordinates).

FIG. 5. Conductivity vs. dilution. 0.02*N* myristic acid in toluene. Oxidation time: 60 min.

Reduction in hydrogen stream (atmospheric pressure, room temperature, platinum-black catalyst) produced a drop in conductivity, as seen in Fig. 4. Hence, it appears that the oxidized ionic species can be, at least partly, converted into reduced, nonionic molecules. Reduction in conductivity was in a ratio of about 1:4 in 60 min, independently of the initial level, which was high for curve 1, moderately high for curve 2.

It was pointed out in earlier papers (1) that the slope of the curve conductivity vs. dilution permits differentiation between electrolytic and oxidation-ions. In the log-log plot the former approaches theoretically a slope of 22.5 degrees, the latter 45 degrees. Fig. 5 gives a dilution curve over a range of four orders of magnitude, the dotted line being a 45 degree slope. Although the experimental curve has not exactly a 45 degree slope, the deviation is not excessive, indicating that the ions in this system are not the result of electrolytic dissociation of a single parent compound.

Aromatic Hydrocarbon

The question arises as to what aromatic hydrocarbons produced the effect observed. Table I gives the results, relating to several aromatics. An increase in conductivity is observable in all cases, it being the most pronounced in toluene. In order to obtain a measurable increase in σ in benzene and xylenes, it was necessary to increase both the ozonizer field and the time. For this reason the figures in the last column offer only qualitative comparison.

At the present stage of the study, and with the mechanism of ion formation as suggested (see later), differences between the various hydrocarbons cannot be explained. Such specific influences of side-chains are, of course, common in many reactions. Methylnaphthalenes, as will be shown in another paper, also produce high conductivities, and so the observations are valid also for condensed aromatic compounds.

Table II presents comparative results on monoalkyl benzene derivatives, indicating decreasing conductivity with increasing complexity of the side chain.

TABLE I. *Comparison of various aromatic hydrocarbons; 0.02N myristic acid; initial conductivity about* 10^{-13} *mho/cm*

Hydrocarbon	Ozonizer field kv/cm	Oxidation time, min	Conductivity, 10^{-13} mho/cm
Benzene	27.3	60	3.8
Benzene	28.0	60	7.5
Toluene	27.3	60	404
Ethylbenzene	27.3	150	91.0
o-Xylene	28.0	120	26.0
o-Xylene	28.3	160	132
m-Xylene	28.0	120	12.0
p-Xylene	28.0	120	12.0
p-Xylene	29.1	250	25.0
Mesitylene	28.7	220	17.6

TABLE II. *Comparison of mono-alkyl benzenes, in solutions of 25% by volume in n-decane; 0.02N myristic acid; ozonizer current 0.15 ma; oxidation time 60 min*

Hydrocarbon	Conductivity, 10^{-12} mho/cm
Toluene	2540
Ethylbenzene	218
n-Propylbenzene	528
n-Butylbenzene	191
sec-Butylbenzene	107
tert-Butylbenzene	76

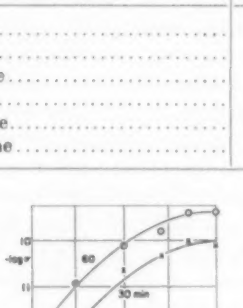


FIG. 6. Conductivity vs. fraction by volume of toluene in a mixture of toluene-*n*-octane. 0.02*N* myristic acid. Oxidation time: 30 and 60 min.

Since the aromatic hydrocarbon is the main source of ions, it was of interest to ascertain the concentration necessary for a positive effect. It was established that aliphatic hydrocarbons as well as saturated rings are ineffective, hence they can be used as diluents (Fig. 6). The relatively small increase in σ with low concentrations of toluene in this instance is caused by its partial evaporation during oxidation. In a solvent of lower boiling point small concentrations are very effective, as will be shown in another paper. Values shown in Fig. 6 are not directly transferable to a mixture of an aromatic with a viscous hydrocarbon oil.

Aliphatic Acid

Some experiments were carried out to determine whether all aliphatic acids would produce ions to the same extent. A number of aliphatic acids of varying chain length were tested (Fig. 7). From valeric to stearic acid the curve passes through a flat maximum at about 12 carbon atoms (lauric acid). However, for acids having fewer than five carbon atoms (valeric acid) the conductivities drop to quite low values.

Fig. 8 shows that about 10 mM/l of acid are needed; above that value, no further increase in σ occurs; below that value, the increase in σ drops sharply. From this it can be seen that about 10 mM/l are involved in the reaction. If the same amount of toluene is involved in the process, it would mean that about 1×10^{-3} mole fraction of toluene undergoes oxidation under the conditions of the experiment.

The bottom curve in Fig. 8 refers to a sample of toluene oxidized without the addition of acid. There is no significant increase in conductivity, and, if the acid is added *after* the oxidation, no significant increase of σ occurs. Thus, the acid does not react with an oxidation product in a manner as it does with amines; it reacts *during* oxidation with some of the intermediates. This latter statement is offered as a hypothesis; it is substantiated, among others (see later), by the following observation. The peroxide of the aromatic compound usually precipitates out because of its limited solubility. If an acid is

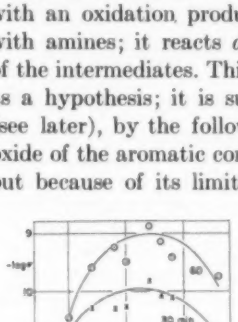


FIG. 7

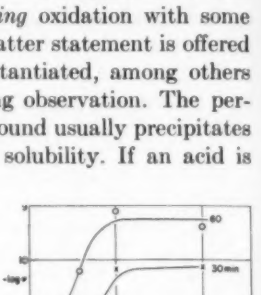


FIG. 8

FIG. 7. Conductivity vs. number of C-atoms of aliphatic acid (0.02*N*) in toluene.

FIG. 8. Conductivity vs. concentration of myristic acid in toluene. Bottom curve: addition of acid after oxidation without acid.

TABLE III. *Additions other than saturated aliphatic acids to toluene, in 0.02N concentration; initial conductivity about 10^{-12} mho/cm*

Compound	Oxidation time, min	Conductivity, 10^{-12} mho/cm
Oleic acid	30	1.0
Benzoic acid	60	1.0
Octadecyl acetate	60	0.05
Tripropionin	30	2.9
Heptaldehyde	60	0.3
Hexyl alcohol	60	1.7
Cetyl alcohol	30	0.1
Cholesterol	60	4050

present during oxidation, precipitation is either completely absent or markedly reduced. This is explainable if it is assumed that the aliphatic acid takes part in the reaction.

In this connection a number of other acids and related substances were tested, the result being shown in Table III. An unsaturated aliphatic acid, oleic acid, is ineffective, as is an aromatic acid, benzoic acid. The ineffectiveness of oleic acid may be explained by its double bond competing with the aromatic for the ozone. Esters, an aldehyde, and alcohols are seen to be equally ineffective. A large conductivity effect was found with cholesterol.

Ultraviolet Absorption Spectra

In order to ascertain the possible reaction mechanism and to find the probable chemical structure of

the ions, absorption spectroscopy was used. By this means some helpful indication, even if no direct evidence, is provided.

Fig. 9 presents the ultraviolet absorption spectra of toluene oxidized by ozone without (curve 1) and with (curve 2) the addition of 0.01*N* myristic acid. In order to eliminate the toluene spectrum, the water extracts of the organic solutions were used for absorption measurements. From the absorption measured in a Beckman spectrophotometer the average product $\overline{\epsilon c}$ was calculated (ϵ = extinction coefficient, c = concentration of compound). Since the concentration of the compounds responsible for absorption was not known, $\overline{\epsilon c}$, i.e., its logarithm, was plotted vs. the wave length λ in millimicrons. This product was calculated from the measured optical density, which is equal to $\epsilon c l$ (l = optical path length). In curve 1 two characteristic peaks appear at 275 and 215 mμ. In curve 2, referring to the sample with acid, additional peaks appear at 335 and 255 mμ.

The basic process on oxidizing aromatics by means of ozone, according to the studies of Harries (2), is ozonide formation. The ozonides undergo cleavage and form diones (3, 4). If diones are formed, their spectrum must be present in the absorption spectrum of the water extract. Glyoxal and methylglyoxal are produced from toluene. As a comparison, an aqueous solution of 2, 3 butanedione was analyzed, the spectrum being given in curve 1 of Fig. 10. With its two peaks at 280 and 205 mμ (the latter to be interpreted with caution because of possible instrument anomalies), it resembles curve 1 of Fig. 9, which is in all probability due to the diones formed from ozonides.

The next point was to determine the kind of compound causing the additional peaks in curve 2, Fig. 9. This point is of particular interest since addition of the aliphatic acid leads to the high concentration of ions. The aliphatic acid itself possesses only one absorption peak near 200 mμ; it does not contribute essentially to the spectrum. Its presence, however, prevents the precipitation of peroxide; the solution remains clear, with a faint yellow color. The acid probably forms a soluble addition compound with the ozonide, the carboxyl group becoming attached to the peroxide group which links two neighboring carbon atoms of the ring. If this conclusion is correct, an aromatic ring with adjacent carbonyl and hydroxyl groups attached ought to be present. A compound approximating such a structure is salicylaldehyde which has a carbonyl and a hydroxyl in ortho position. The spectrum of the latter (5) is shown as curve 2 in Fig. 10; it has peaks at 325 and 255 mμ. The location of these peaks agrees fairly well with the two additional peaks found in curve 2, Fig. 9. Thus, the absorption spectra are in agreement with the assumption of an addition compound formed by the aromatic hydrocarbon and the aliphatic acid. This compound is thought of as an intermediate product which oxidizes further in the course of the reaction. A fraction of it might dissociate into an aliphatic anion and an oxonium cation such as postulated in the previous studies. These ions, being relatively stable, might persist for some time, as was observed. The role of the acid, as here assumed, is verified by further experiments discussed in the following section.

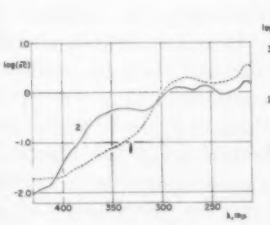


FIG. 9

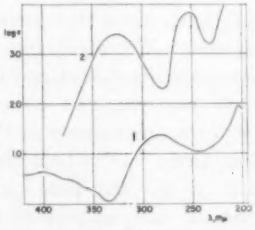


FIG. 10

FIG. 9. Extinction coefficient vs. wave length λ in millimicrons. Curve 1, toluene, oxidized by O_3 for 8 min; Curve 2, 0.01*N* myristic acid in toluene, oxidized by O_3 for 8 min.

FIG. 10. Extinction coefficient vs. wave length. Curve 1, 2-3 butanedione in water; curve 2, salicylaldehyde in alcohol (Kiss and Nyiri).

TITRATION AND PRECIPITATION OF ACID

In order to clarify further the role of the aliphatic acid, total acidity was measured by titration.

The role of the aliphatic acid is of considerable interest from the standpoint of electrical insulation inasmuch as its connection with deterioration of oils is known (6). In this particular instance the acid is clearly the cause of high electrical conductivity due to the formation of oxidation ions.

Aliphatic acids are generally resistant to oxidation and it was therefore not expected that in the course of the reaction studied they should form low molecular, water-soluble acids. In order to check this, titration of toluene-myristic acid samples was carried out; the result is presented in Table IV. The titration was carried out in alcoholic system, with

TABLE IV. *Titration results in ozone oxidation*

Hydrocarbon	Myristic acid	Oxidation time, min	Normality of total acid		
			Original solution	Oxidized solution	Water extract of latter
n-Octane	+	30	0.019	0.020	0.001
Cyclohexane	+	30	0.019	0.020	0.000
Toluene	−	15	0.000	0.010	0.006
Toluene	+	15	0.019	0.027	0.005
Toluene	−	30	0.000	0.031	0.026
Toluene	+	30	0.020	0.058	0.024

alcoholic $N/50$ KOH as titrating agent and alkali blue as indicator. The first two samples, containing indifferent solvents with acid, show that the latter does not produce additional acidity and, in particular, no water-soluble acids are formed. The third sample, toluene, yields 10 mM/l of acid as secondary product, a large part of which is water soluble. If myristic acid is added prior to oxidation, the amount of excess (8 mM/l) and its water-soluble fraction are about the same as in the case without acid, showing that the latter does not affect the reaction as far as production of new acid is concerned. The last two samples with excess acid concentrations of 31 and 28 mM/l confirm the result.

The assumption of an addition compound formed by the aromatic and the acid as a precursor of ions, indicated by the absorption spectra, is strengthened by two further experiments.

If the acid forms an addition compound at the carboxyl group, then binding the latter prior to oxidation should reduce the ionic effect. Amines, by forming soluble salts, bind the carboxyl group of aliphatic acids. Fig. 11 shows the result of this test. The lower curves show that conductivity markedly decreases upon the simultaneous addition of tributyl amine. There are no significant changes in σ on adding amine after oxidation since the main action of the acid takes place during oxidation.

If the conclusion that the acid forms an addition compound with an aromatic intermediate is correct, it should be more difficult to form salts of the aliphatic acid after oxidation than before. A visible criterion of salt formation is the precipitation of a white crystalline powder after addition of an equivalent amount of KOH in alcoholic solution. Prior to oxidation such visible precipitates were found to form. After oxidation, either no precipitate or only traces of crystals were formed; sometimes after an hour more precipitate was observed. As a control of such tests additional acid was dissolved in the samples after oxidation, leading to prompt precipitation with KOH. These data are summarized in Table V, and indicate that the acid, as a result of the reaction, was not in an entirely free state. While

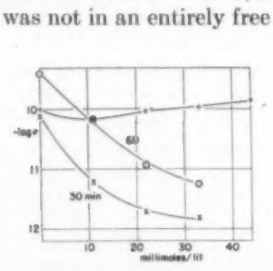


FIG. 11. Conductivity vs. concentration of tributylamine during oxidation. Top curve: addition of amine after oxidation.

TABLE V. *Precipitation by* KOH *of the potassium salt of aliphatic acid*

Acid	Normality	Oxidation time, min	% alcohol during precipitation	Precipitate of potassium salt	
				Without further addition of acid	With further addition of acid
Tridecanoic	0.02	15	25	−	+
Myristic	0.02	10	25	−	+
Palmitic	0.01	10	10	−	+
Stearic	0.01	15	10	−	+

the acid remained in a state to be titrated, precipitation of the potassium salt was delayed markedly. This might be explained on the basis of an acid-peroxide addition compound, held together by a loose electron pair. In analogy to the case of acid-amine compounds previously studied (7), dissociation to a small extent into ions (negative aliphatic and positive oxonium ions) is a possible result of such compound formation.

PARAMAGNETIC SUSCEPTIBILITY OF RADICALS

Oxidation-ion formation may be preceded by the occurrence of free radicals as was indicated in the case of orthodiols. Quite generally, radicals are assumed as intermediates in the cleavage of the —O—O— group (8). McLean (9) explains the action of inhibitors by their capture of radicals that occur under the action of the electrical discharge in dielectrics. In the present instance it is possible that the peroxide group in the ozonide cleaves by forming two unshared electrons in the aromatic molecule, the process being followed by addition of the aliphatic acid. While the majority of organic radicals is short-lived, there are others which are more or less stable and accessible to paramagnetic measurements (10). In fact, the paramagnetic technique (11), besides other methods, has been used extensively in the study of free radicals in usual organic solvents. Since the concentration of radicals or biradicals, if present, must be relatively large, it was attempted to detect and measure them by means of their paramagnetic susceptibility. This was done by the magnetostatic method, as devised by Quincke and Gouy (12). This method gives the algebraic sum of all the para- and diamagnetic moments present, and, as pointed out by Hutchison (13), is subject to error on this account. The paramagnetic resonance method as used by that author, among others, is free of this drawback. Since the total diamagnetic susceptibility might increase in the course of a reaction, the paramagnetic susceptibility as calculated from the static method is the lower

limit of a range and may be subject to a correction upward.

The method is based on the principle that a solution is attracted or repelled by a static magnetic field according to the sign of its susceptibility. All organic molecules are diamagnetic, except free radicals, the paramagnetic molar susceptibility χ_m of which for one unshared electron is 1300×10^{-6} cgs units. If radicals are produced in the course of oxidation, the oxidized sample should show a lesser repulsion than the original solution, the difference being a measure of the amount of radicals.

The solution of susceptibility κ and density ρ was contained in a U-tube having a narrow and a wide leg, the narrow leg being between the poles of an electromagnet. In switching on the field H (in Gauss), the meniscus level, observed by a microscope, was lowered by h cm in accordance with the relation

$$h\rho g = 0.5\ \kappa H^2$$

In this simplified equation g = gravitational constant. Since κ for toluene is 0.63×10^{-6} and H was approximately 15,000 Gauss, by computation h is 86×10^{-3} cm; this value was confirmed by experiment. After oxidation the change in level was found to be somewhat less; the difference between the two being Δh.

If the molar fraction of radicals in toluene is denoted by $r (r \ll 1)$, then the corresponding susceptibility is $1300 \times 10^{-6}\ r$. The molar susceptibility of toluene (molecular weight = 92, density = 0.87 g/cc) is $92 \times 0.63 \times 10^{-6}/0.87 = 66 \times 10^{-6}$, and the relative change due to radicals is $1300 \times 10^{-6}\ r/66 \times 10^{-6} = 20\ r$. From the equation above the approximate relation $\Delta h/h = 20\ r$ can be deduced, hence

$$r = 0.05\ \Delta h/h$$

Fig. 12 shows the test results as a plot of $\Delta h/h$ vs. oxidation time. The precision of these measurements is moderate, but the order of magnitude of the difference observed was consistent. The crosses refer to control measurements made under the same conditions with the exception that the indifferent solvent *n*-octane was used instead of toluene. As can be seen, $\Delta h/h$ was about 0.04 for toluene, and zero for *n*-octane. From the equation above, a value of $r = 2 \times 10^{-3}$ follows, i.e., about 0.2% toluene was present in the form of radicals immediately after oxidation. If biradicals are assumed to exist, this value would be about 0.1%. This order of magnitude is comparable with the 0.1%, previously arrived at, as the percentage of toluene involved in the reaction.

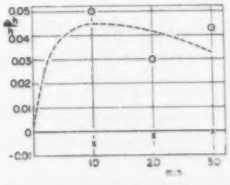
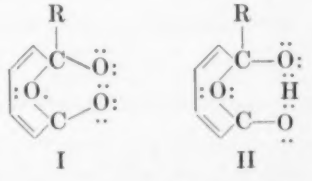


FIG. 12. Relative change in level in paramagnetic measurements vs. oxidation time. ○ toluene, 0.02*N* myristic acid, × *n*-octane.

As for the cations formed on dissociation of the toluene-acid complex, it can be assumed that they are of the oxonium type. Structure I indicates the ozonide formed from a mono-alkyl benzene, and structure II indicates an oxonium cation upon addition of a proton. The formula is written for a monomer; actually the ion might be a dimer, tetramer, or the like. The ionic structure has additional stability due to the six-membered ring containing the proton. Either of the two oxygen atoms to the right could take up the additional pair of electrons, and this possibility of resonance stabilizes the ionic structure.



Structure II has a similarity with the semiquinone type of cation postulated previously as a result of the oxidation of catechol. These ionic structures need, of course, further verification.

The concept of ion pairs of the kind considered is perhaps unusual. The existence of aliphatic acid anions in hydrocarbons in the presence of amines was shown by the writer in a quantitative manner, by means of a radioactive tracer technique (14). The existence of oxonium cations as reaction intermediates from peroxides as well as other compounds is frequently assumed (15). The observations in this study are interpreted as an instance in which the presence of such ions is demonstrated owing to their electrical conductivity.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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Electrodeposition of Molydenum Alloys from Aqueous Solutions[1]

D. W. Ernst, R. F. Amlie, and M. L. Holt

Chemistry Department, University of Wisconsin, Madison, Wisconsin

ABSTRACT

Nickel-molybdenum, cobalt-molybdenum, and iron-molybdenum alloys have been electrodeposited from aqueous solutions containing sodium molybdate, the sulfate of the codeposited metal, sodium citrate, and ammonium hydroxide. Typical baths were made up with 0.3 M/l of the codepositing metal sulfate, 0.3 M/l of sodium citrate, varying amounts of sodium molybdate, and ammonium hydroxide to *p*H about 10.5. The maximum amount of molybdenum in the electrodeposited alloys depends on the alloying metal. When a typical bath was used, nickel alloys were found to contain up to 20% molybdenum, cobalt alloys contained up to 40% molybdenum, and iron alloys contained about 50% molybdenum. The cathode current efficiency in the above cases ranged from 75–85% for the nickel-molybdenum bath, 50–60% for cobalt-molybdenum, and 10–20% for iron-molybdenum. The effects of *p*H, concentration, temperature, and cathode current density on cathode current efficiency and alloy composition were studied.

These electrodeposited molybdenum alloys were metallic and either bright or light gray in appearance, with a large number of cracks in the bright deposits. Adherence of the deposit to well-cleaned flat cathodes seemed to be good, but adherence to tubing or rods was poor; usually these deposits could be brushed off in flake or powder form.

Introduction

The electrodeposition of molybdenum alloys containing iron, cobalt, or nickel has been reported previously from this laboratory (1) and a patent has been issued (2). Yntema and Ksycki (3, 4) described the use of solutions containing either aliphatic acids or their salts, or various fluorides to electrodeposit molybdenum alloys. Brenner and Burkhead (5) electrodeposited cobalt-molybdenum alloys from strongly alkaline solutions containing potassium carbonate, cobalt chloride, and sodium molybdate. Ma (6) described the electrodeposition of chromium-molybdenum alloys from a regular chromium plating bath containing molybdenum-(VI) oxide. A ternary alloy consisting of molybdenum, tungsten, and cobalt has been electrodeposited from aqueous citrate solutions by McElwee and Holt (7). The electrodeposition of nickel-molybdenum alloys from tartrate and citrate baths has been reported recently (8).

Seim and Holt (1) prepared their plating solutions using sodium molybdate, the sulfate of the codepositing metal, citric acid, and ammonium hydroxide. In this work sodium citrate was used in place of citric acid, being chosen after studying several different complexing agents. An attempt was also made to find another reagent for adjusting the *p*H of the plating solutions because of the volatility of ammonia.

Experimental Methods and Results

The methods used were similar to those described previously (1) except that in some cases $Na_2MoO_4 \cdot 2H_2O$ was used instead of anhydrous Na_2MoO_4. The volume of plating solution used for each electrolysis was 250 ml.

In analyzing cobalt-molybdenum and nickel-molybdenum deposits, the codeposited metal was always determined and molybdenum was usually found by difference. Occasionally molybdenum was determined by the lead molybdate method (9). When both metals were determined the analysis usually totaled 98% or more. Several of the nickel-molybdenum deposits were heated in hydrogen to about 850°C and showed a loss in weight of only 0.5%. Very few of the deposits obtained from the Fe-Mo bath were completely metallic, being covered in the center with a dark black material believed to be a molybdenum oxide; because of this, both components of these alloys were determined, and the total percentage varied from 80–95%, depending on the molybdenum content of the deposit. When several of the iron-molybdenum alloys were heated in hydrogen at about 850°C, the resulting loss in weight was 8 to 9% and the total analysis was then close to 100% (8.2% loss in weight, 40.0% Fe, 51.6% Mo).

Cathode current efficiencies were calculated using

[1] Manuscript received September 4, 1953. This paper was prepared for delivery before the Wrightsville Beach Meeting, September 13 to 16, 1953.

the analysis and the equivalent weights based on the oxidation states Mo(VI), Ni(II), Co(II), and Fe(II). Calculations of C.C.E. based on Fe(III) and Co(III) were made and generally found to be 10–20% higher than those based on the bivalent state, and some efficiencies for the Co-Mo plating solutions were over 100%.

The *p*H of the plating solutions was determined using a Beckman model G *p*H meter and a glass electrode. No attempt was made to correct for salt effects.

Hull Cell Studies

The Hull cell described previously (1) was used to compare the nickel-molybdenum plating baths which contained different complexing agents. Cathode plates were obtained by electrolysis at 3 amp for 2 min and compared as to gain in weight and deposit appearance over the current density range of approximately 1–20 amp/dm². Plating solutions used for this investigation had the composition: 0.3 M/l of nickel sulfate; 0.3 M/l of the complexing agent; variable amounts of sodium molybdate; and a *p*H of about 10.5 with ammonium hydroxide. The concentration of 0.3 M/l was selected after numerous preliminary experiments as being the most suitable for the objectives in mind.

As a result of the Hull cell studies the complexing agents were classified as either poor or good for the electrodeposition of nickel-molybdenum alloys. Some of the complexing agents found to be good were: sodium citrate, sodium-potassium citrate, Rochelle salts, and sodium tartrate. For plating cobalt-molybdenum alloys the good complexing agents were: sodium citrate, malic acid, sodium malate, glycolic acid, and citric acid. Other complexing agents used were gluconic acid, dextrose, malonic acid, versene, oxalic acid, and the sodium and ammonium salts of some of these acids.

A schematic representation of Hull cell cathodes from a series of sodium citrate solutions classified "good" is given in Fig. 1 and in a similar manner those from a "citric acid" bath[2] classified "poor" is given in Fig. 2. Differences in the weights of the deposits as given in Fig. 1 and 2 should be noted particularly as an indication of changes in approximate current efficiencies.[3]

[2] Citric acid is used as the source of citrate ion and is neutralized by the ammonium hydroxide when the bath is prepared.

[3] Work in this laboratory indicates that the deposit weight on the Hull cell cathode is reproducible if all conditions of the deposition process are kept constant (i.e., constant amperage, time interval, temperature, etc.). Individually made up Watts' baths used in a Hull cell (3 amp, 110 sec, 43°C, *p*H 1.8) gave the following deposit weights: 90.6, 90.9, and 91.5 mg.

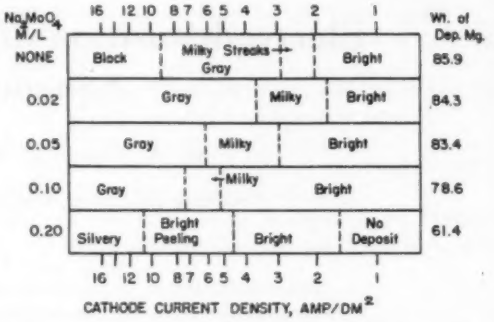


FIG. 1. Appearance of Hull cell cathodes, showing the plating range of sodium citrate nickel-molybdenum solutions containing varying amounts of sodium molybdate (3 amp for 2 min at room temperature; *p*H 10.5).

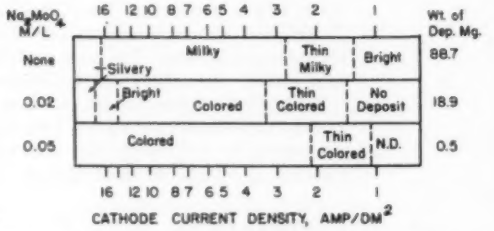


FIG. 2. Appearance of Hull cell cathodes, showing the plating range of "citric acid" nickel-molybdenum solutions containing varying amounts of sodium molybdate (3 amp for 2 min at room temperature; *p*H 10.5).

Regular Plating Procedures

Regular plating procedures were used to obtain more quantitative information about C.C.E. and alloy compositions from various citrate Ni-Mo baths. Results are given in Table I.

Table I shows that, for the Ni-Mo bath, the presence of NH_4^+ or K^+ appears to limit the amount of Na_2MoO_4 which can be added before the C.C.E. drops off appreciably. However, for a given concentration of Na_2MoO_4, a larger percentage of molyb-

A series of Hull cell runs made on 250 ml aliquots of a citric acid nickel bath at various *p*H values showed the following

Bath No.	Bath *p*H	Wt of deposit, mg Run 1	Wt of deposit, mg Run 2
1	1.3	9.0	9.7
2	6.5	54.5	55.6
3	9.5	81.9	81.4

If the above baths were judged only by deposit appearance, then baths 2 and 3 compare favorably with each other and there would be no basis for using one instead of the other; whereas, if the deposit weights are available, bath 3 can be chosen because it has good appearance and a higher C.C.E. Thus as an additional aid in determining the suitability of various complexing agents, the weight of the deposit should be considered. Baths could be regarded as having the same C.C.E. if the deposit weights agreed to within 1 or 2 mg.

TABLE I. *Comparison of nickel-molybdenum citrate plating solutions containing increasing amounts of sodium molybdate*

(0.3 M/l $NiSO_4$; 0.3 M/l citrate; NH_4OH to *p*H 10.5; 25°C; 10 amp/dm² for 10 min)

	Bath			
Na_2MoO_4	Na_3 citrate	$(NaK)_3$ citrate*	K_3 citrate	$(NH_4)_3H$ citrate
M/l	C.C.E. %	C.C.E. %	C.C.E. %	C.C.E. %
None	82	80	85	82
0.02	82	79	82	10
0.05	81	80	51	3
0.1	80	78	Nil	Nil
0.2	78	81	Nil	Nil
	Ni in alloy	Ni in alloy	Ni in alloy	Ni in alloy
	per cent	per cent	per cent	per cent
None	100.0	100.0	100.0	100.0
0.02	98.3	95.6	95.6	89.5
0.05	95.9	91.7	83.4	77.0
0.1	92.6	84.3	—	—
0.2	86.7	79.4	—	—

* 0.15 M/l Na_3 citrate + 0.15 M/l K_3 citrate.

TABLE II. *Effect of increasing amounts of ammonium citrate (and corresponding decrease of sodium citrate) on the nickel-molybdenum plating solution*

Electrolysis for 10 min at 10 amp/dm²; *p*H about 10.5; room temperature

Citrate–0.3 M/l		Cathode deposit	Approx. C.C.E.	Nickel in deposit
Na_3 Cit	$(NH_4)_2HCit$			
		g	%	%
0.3 M/l	0.0 M/l	0.2383	82	86.1
0.25 M/l	0.05 M/l	0.1682	58	79.6
0.20 M/l	0.1 M/l	0.0208	8	69.2
0.15 M/l	0.15 M/l	0.0088	—	—
0.10 M/l	0.20 M/l	0.0057	—	—
0.0 M/l	0.3 M/l	0.0045	—	—

denum is obtained in the alloy deposit from baths containing these same two ions.

The observation that Ni-Mo plating solutions prepared from citric acid and ammonium hydroxide to *p*H 10.5 gave much lower C.C.E. than similar solutions prepared from sodium citrate suggested that it was the excess ammonium salts present in the former solutions which caused the lower C.C.E. The effect of ammonium ion was studied by using plating solutions with the standard concentration but with the 0.3 M/l of citrate ion supplied by varying amounts of sodium citrate, Na_3Cit, and ammonium citrate, $(NH_4)_2HCit$. The results, in Table II, show that increasing the ammonium ion concentration decreases both the C.C.E. and the nickel content of the alloy deposit. The same effect was noted for the cobalt-molybdenum citrate bath.

Sodium Citrate Bath

The early work on Ni-Mo plating solutions did not indicate that the sodium citrate bath was better than, for example, a Rochelle salt bath, although the tartrate solutions had the disadvantage of forming a precipitate over the approximate *p*H range of 3.0–9.0. There is, however, no question about the superiority of sodium citrate as the complexing agent over citric acid or ammonium citrate for the deposition of molybdenum alloys. Extensive work had been done with the Ni-Mo citrate bath at the time that the study on the Co-Mo plating baths was started, and when sodium citrate was also found to be a "good" complexing agent, it was decided that a comparison of the electrodeposition of three alloys, iron-molybdenum, cobalt-molybdenum, and nickel-molybdenum from sodium citrate solutions, should be made.

Bath.—The alloy deposits compared were electrodeposited using the following bath concentrations and conditions unless otherwise stated:

Sulfate of codepositing metal	0.3 M/l
Sodium citrate	0.3 M/l
Sodium molybdate	0.2 M/l
Ammonium hydroxide	to *p*H 10.5
Current density	10 amp/dm²
Time of electrolysis	10 min for nickel and cobalt alloys and 20 min for iron alloys
Temperature	25°C
Volume of solution	250 ml

These conditions were used for the Co-Mo and Fe-Mo baths even though they are probably not the best conditions for this purpose. No difficulty was encountered in the preparation of the plating solutions; however, the Fe-Mo solution was allowed to stand for several hours before use to help obtain consistent results. Some of the Fe-Mo baths had solid material settling out upon long standing.

Bath temperature.—A heating coil was used to maintain the bath at elevated temperatures during electrolysis. Measurements of *p*H were made at the operating temperature of the bath using a high temperature glass electrode. The results of electrolysis at three temperatures are given in Table III.

This table shows that increasing the bath temperature decreases the percentage of iron and nickel in the alloys, but increases the amount of cobalt. The molybdenum content of the iron-molybdenum alloys remained nearly constant. The fact that the iron and nickel content of the deposit decreases (the opposite would be expected) may be accounted for by the *p*H change of the bath. The *p*H of the Fe-Mo and Ni-Mo baths at 70°C is approximately a whole unit lower than at 30°C and Fig. 9 shows the percentages of codepositing metals to be approximately 32% iron and 71% nickel at the lower *p*H values. Thus, the percentage of iron and nickel is increased (36.8%; 78.8%) due to an increase in temperature,

TABLE III. *Effect of bath temperature on the sodium citrate molybdenum alloy bath*

Bath temp	Approximate bath pH	Bath C.C.E. %			% Codeposited metal		
		Fe-Mo	Co-Mo	Ni-Mo	Fe	Co	Ni
°C							
30	10.5	16	51	84	39.6	55.9	83.4
55	10.3–9.9	11	79	86	37.1	75.3	79.7
70	10.0–9.5	6	86	85	36.8	74.5	78.8

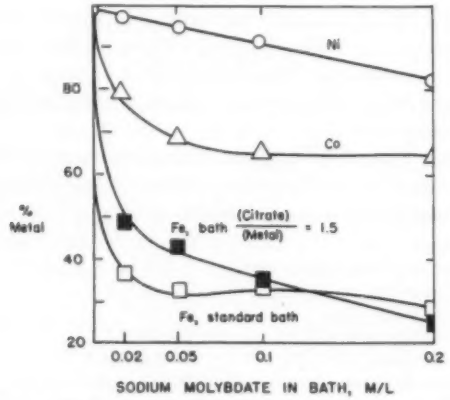


FIG. 3. Effect of sodium molybdate bath concentration on the composition of molybdenum alloys from sodium citrate molybdenum alloy baths.

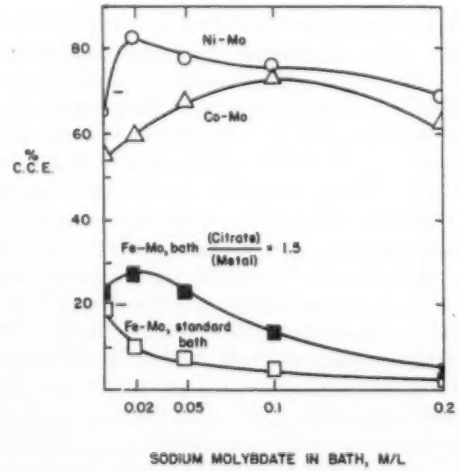


FIG. 4. Effect of sodium molybdate bath concentration on the cathode current efficiency of sodium citrate molybdenum alloy baths.

when the correction for *p*H is applied. It can be seen that at the higher temperature the C.C.E. of the Fe-Mo bath decreased, the efficiency of the Co-Mo bath increased, and there was slight effect upon the Ni-Mo bath.

Concentration of sodium molybdate.—Fig. 3 and 4 show the effect that the concentration of sodium molybdate has on the three sodium citrate solutions.

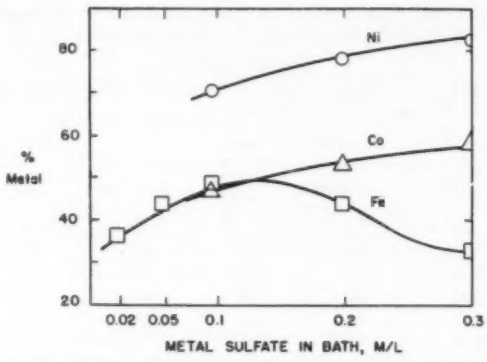


FIG. 5. Effect of concentration of metal sulfate on composition of molybdenum alloys from the sodium citrate molybdenum alloy baths (Fe-Mo bath, 20 amp/dm², 0.1 M/l $Na_2MoO_4 \cdot 2H_2O$).

An increase of molybdate has the expected result of decreasing the percentage of iron, cobalt, or nickel in the alloy (Fig. 3) and increasing the molybdenum content. The percentage of molybdenum in the alloy deposit when small amounts of molybdate (0.02 to 0.05 M/l) are added to a bath is found to increase most rapidly in the iron-molybdenum alloy and least rapidly in the nickel-molybdenum alloy (Fig. 3). Fig. 4 shows that the C.C.E. increases and then decreases for the Co-Mo and Ni-Mo baths as the sodium molybdate concentration is increased. The efficiency for the Fe-Mo bath decreases from the start; however, if the citrate ion concentration is 1.5 times the iron concentration, there is an increase in the efficiency and then a decrease, similar to the Ni-Mo bath.

Concentration of codepositing metal sulfate.—The results of the electrolysis of a series of sodium citrate baths containing increasing amounts of metal sulfate are given in Fig. 5 and 6. Fig. 5 shows that the percentage of cobalt and nickel increases as their bath concentration increases, while the iron content of the alloy increases and then decreases as the iron sulfate concentration in the bath increases. The molybdenum content of the alloy decreases as the codepositing metal concentration increases; however, in the iron bath the molybdenum content increases at higher metal concentration. It is shown in Fig. 6 that the C.C.E. increases as the metal concentration is increased, and again the Fe-Mo bath has a lower C.C.E. when the iron sulfate concentration is high. It may be significant to note that an Fe-Mo bath, having a molar ratio of citrate to iron of 1.5, acts much like the Co-Mo and Ni-Mo baths. Note especially in Fig. 4 the effect that the concentration of sodium molybdate has on the C.C.E. of the Fe-Mo bath where the citrate concentration was 1.5 times the iron sulfate concentration.

Concentration of sodium citrate.—The results of the

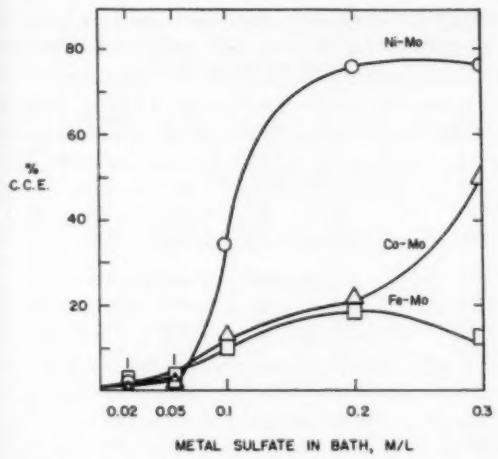


FIG. 6. Effect of concentration of metal sulfate on cathode current efficiency of sodium citrate molybdenum alloy baths (Fe-Mo bath, 20 amp/dm², 0.1 M/l $Na_2MoO_4 \cdot 2H_2O$).

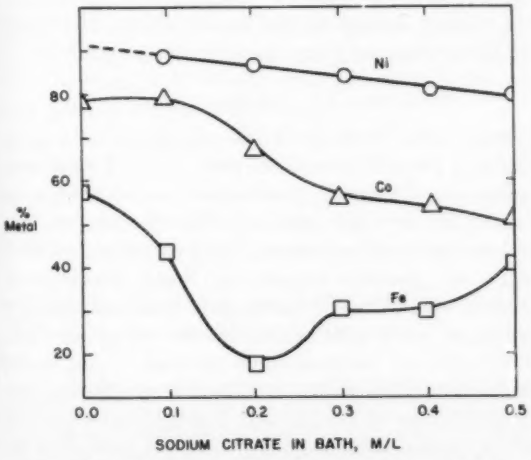


FIG. 7. Effect of concentration of sodium citrate on composition of molybdenum alloys from sodium citrate molybdenum alloy baths.

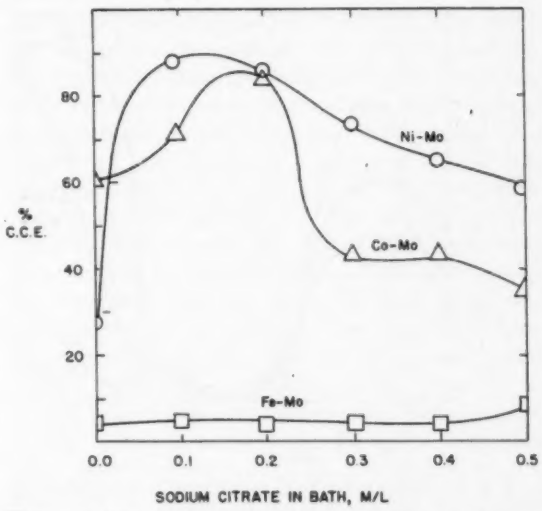


FIG. 8. Effect of concentration of sodium citrate on cathode current efficiency of sodium citrate molybdenum alloy baths.

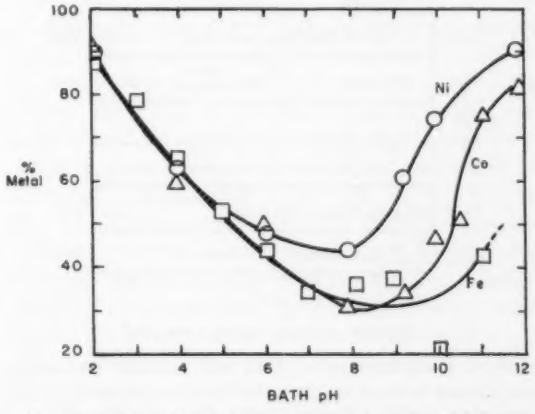


FIG. 9. Effect of bath *p*H on composition of molybdenum alloys from sodium citrate molybdenum alloy baths.

electrolysis of a series of plating solutions containing increasing amounts of sodium citrate are given in Fig. 7 and 8. It can be seen in Fig. 7 that the percentage of cobalt and of nickel in the alloys decreases and the percentage of iron decreases and then increases as the citrate concentration is increased. Other work with the Fe-Mo bath indicates that the iron content of the alloy steadily increases and that the molybdenum content increases and then decreases as the citrate content of the bath increases. The C.C.E. (Fig. 8) for the Ni-Mo and Co-Mo baths increases and then decreases while in the Fe-Mo bath it is nearly constant at mole ratios of citrate to iron below 1.5 (<0.5 M/l Na_3 citrate).

Bath pH.—All three plating solutions were studied over the *p*H range 2.0 to about 12.0. The *p*H was adjusted downward with dilute H_2SO_4 and upward with NH_4OH. The *p*H in each case is the value given by the glass electrode (uncorrected). The results of the electrolysis of solutions at the various *p*H values are given in Fig. 9 and 10. In general it can be said that the iron, cobalt, and nickel content of the alloys decreased and then increased as the *p*H is increased (Fig. 9). The percentage of iron, cobalt, and nickel in the alloys from baths below *p*H 7.0 is nearly the same, while at higher *p*H values the three metals are present in widely different percentages; this effect of *p*H at the higher *p*H values may be due to the complexing action of NH_3 and not to the OH^- concentration. The lowest amount of codeposited metal in nickel-molybdenum and cobalt-molybdenum alloys occurs at approximately *p*H 8.0 while it

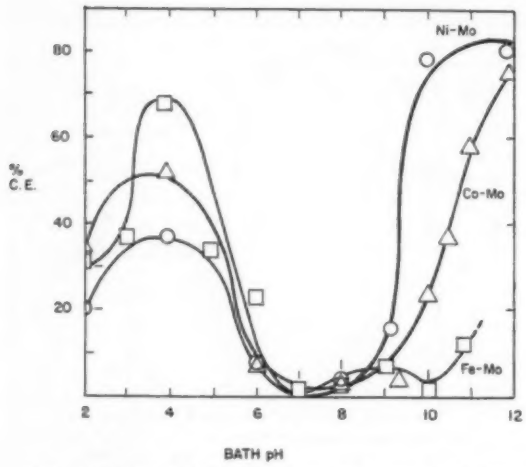


FIG. 10. Effect of bath *p*H on cathode current efficiency of sodium citrate molybdenum alloy baths.

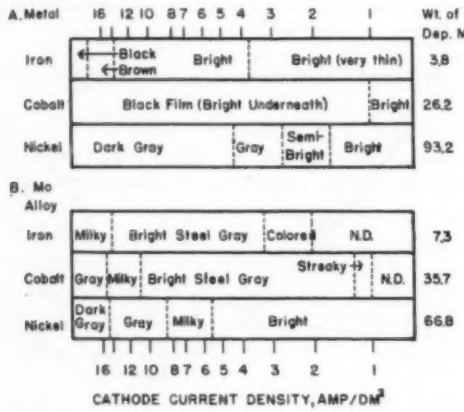


FIG. 11. Appearance of Hull cell cathodes comparing the plating range of a plain sodium citrate metal bath, (A), and of a sodium citrate alloy bath containing 0.1 M/l sodium molybdate, (B) (3 amp for 2 min; *p*H 10.5; room temp).

is lowest at *p*H 9.0 in the iron-molybdenum alloys. The percentage of molybdenum is highest at approximately the same *p*H values. Fig. 10 shows that at a *p*H of 7 to 8 a minimum in C.C.E. is obtained, while at *p*H 4 and *p*H 10–10.5 a maximum is obtained. At the higher *p*H the Ni-Mo bath operates with the highest C.C.E. followed by the Co-Mo and Fe-Mo baths, while at the lower *p*H the order is reversed with the Fe-Mo bath operating with the highest C.C.E.

Cathode current density.—The over-all effect of current density is best observed by means of the Hull cell. Fig. 11 shows Hull cell cathodes obtained from some of the baths studied.

More quantitative information was desired and regular plating procedures at several cathode current densities were tried with the results given in Table IV.

TABLE IV. *The effect of cathode current density (C.C.D.) on cathode current efficiency (C.C.E.) and alloy composition using the sodium citrate bath*

Bath	C.C.D.	Time	Wt. of deposit,	Approx. C.C.E.	% Codeposited metal in deposit
	amp/dm²	*min*	*g*	%	
Fe-Mo	10	20	0.0242	2.5	28.5
Fe-Mo	20	20	0.0436	4.0	32.1
Co-Mo	1	100	0.0016	0.4	—
Co-Mo	5	20	0.0616	26	50.8
Co-Mo	10	10	0.0766	30	54.8
Co-Mo	20	5	0.1175	47	66.8
Ni-Mo	1	100	0.0852	34	71.8
Ni-Mo	5	20	0.1904	70	80.0
Ni-Mo	10	10	0.2299	82	83.2
Ni-Mo	20	5	0.2210	76	86.4

It is to be noted that the percentage of codepositing metal in the alloy increases somewhat as the current density increases. The C.C.E. increases with increasing current density for the Fe-Mo and Co-Mo baths and after increasing decreases for the Ni-Mo bath.

Substitutes for Ammonium Hydroxide

Since NH_4OH is a volatile base, its use in a plating bath should be avoided, particularly if an excess appears to be needed; thus numerous substitutes for raising the bath *p*H were tried. The standard sodium citrate bath without ammonium hydroxide was used with the possible substitutes. Small amounts of NaOH were added to portions of this bath to give solutions with *p*H values in the range 7–11.0. Electrolysis of these solutions resulted in only small cathode deposits with C.C.E. less than 1%. Various combinations of NaOH and NH_4OH gave plating solutions that showed good C.C.E. only with a large excess of NH_4OH. The following other substitutes were tried: ethyl amine, ethanol amine, diethanol amine, triethanol amine, ethylenediamine, pyridine, and hydrazine. In no case was a suitable plating bath obtained. Later, the above experiments were conducted on the Co-Mo plating bath and the results obtained for the Ni-Mo bath confirmed.

Anodes

Insoluble platinum anodes were used in all electrolyses reported in this article, but soluble anodes are likely to be required for proper maintenance of the plating solutions. Exploratory work on the Ni-Mo bath with soluble anodes indicates that, whereas Mo anodes dissolve readily, changes in bath composition are required before Ni anodes will dissolve sufficiently to maintain the nickel concentration of the bath. Ni anodes used in the sodium citrate bath, *p*H about 10.5, dissolve only slightly with anode

efficiencies less than 1%. As would be expected the addition of chloride ion, as NaCl, $MgCl_2$, or $NiCl_2$ increases the rate of anode dissolution. An increase in the anode current density was also found to increase the anode current efficiency in solutions containing chloride ions. Molybdenum anodes were found to dissolve with an efficiency of 95 to 100%.

Examination of Deposits

All the deposits which were examined were metallic in appearance. Some of the iron-molybdenum deposits were nonmetallic, but the properties of such deposits are not included in this paper. The nickel-molybdenum alloys were either silvery or gray in appearance and were bright when plated on polished cathodes. The cobalt-molybdenum alloys were either gray, silvery, or bright; in some cases the alloy was bright even though the basis metal was not polished. The iron-molybdenum alloys had the appearance of gray cast iron and no bright deposits were obtained. The alloy deposits examined usually ranged up to 0.0004 in. in thickness, but somewhat thicker deposits can be obtained. Alloys were readily soluble in 4*N* nitric acid which was used to dissolve the deposits for making analyses.

All of the deposits contained cracks (see Fig. 12), the brigher the deposit the more and finer the cracks (the surface has a spider web appearance). Iron-molybdenum deposits contained the fewest cracks, while the bright cobalt-molybdenum deposits had the most.

Adhesion of the deposits to flat cathode surfaces was good, but occasionally the deposit peeled in spots and careful handling of the cathode after cleaning was necessary. In most cases adhesion was not good when the alloys were deposited on steel rods, or on copper or brass tubing. Such deposits were easily rubbed off in a flake or powder form, but in a number of cases a very thin layer (see Fig. 12) adhered strongly to the basis metal with the bulk of the deposit separating from this thin coating and not from the basis metal. Removal of the copper tube from some of the better nickel-molybdenum deposits by chemical means left a fragile shell which was porous and easily crumbled. Deposits plated on stainless steel cathodes were shriveled in appearance and could be brushed off in flake or powder form.

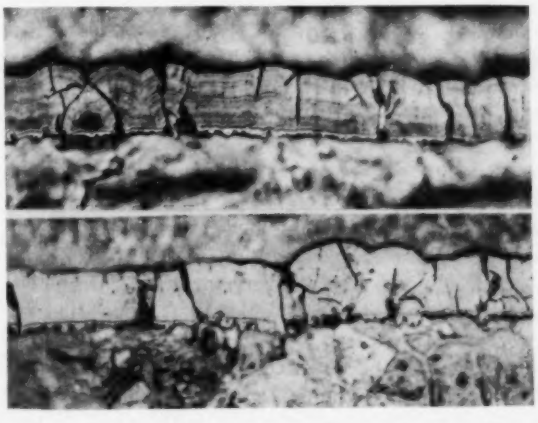


FIG. 12. Micrographs (500 ×) of typical nickel-molybdenum alloy deposits as plated on a copper tube, and then covered with copper electrodeposited from a cyanide bath. Etch: 2-min immersion in a H_2SO_4-H_2O_2 solution (2 ml 98% H_2SO_4, 10 ml 30% H_2O_2; 100 ml H_2O) at 30°C. The deposit is nodular, contains many cracks, and has a banded structure. Preferential etching of copper causes copper portions of micrograph to be out of focus.

The alloy deposits on copper, when bent once 90° or 180°, cracked, usually along the initial crack lines showing the copper basis metal. The amount of copper exposed depended upon the size and distribution of the initial cracks, the many smaller spaced cracks showed less basis metal than the fewer larger spaced cracks. The adhesion of the nickel-molybdenum alloys to the basis metal during repeated bending was good and the alloy did not flake off until the cathode metal was nearly broken. The iron-molybdenum alloys after several bends began to flake off in areas around the bend. The cobalt alloys withstood the bending test better than the iron-molybdenum alloys but not as well as the nickel-molybdenum alloys.

The poor character of most of the deposits may be due to the hydrogen which was deposited on the cathode. Very little hydrogen is evolved from the cathode during plating but when the deposits (especially the iron-molybdenum and cobalt-molybdenum deposits) were washed, large amounts of gas were evolved. This absorbed hydrogen perhaps caused stresses in the alloy deposits and caused the shriveled appearance of the deposits when plated on the flat stainless steel and on the tubing.

DISCUSSION

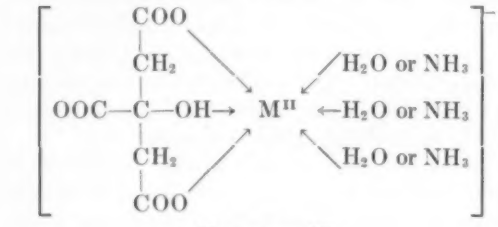
The results presented make it reasonable to conclude that a practical aqueous plating bath for the electrodeposition of molybdenum alloys containing iron, cobalt, or nickel could be worked out. However, the development of such a plating bath was not the immediate objective of this work.

It was found that the Ni-Mo citrate bath operates much more efficiently (C.C.E. 75–85%) than either the Co-Mo (C.C.E. 50–60%) or the Fe-Mo (C.C.E. 10–20%) citrate baths, while a higher molybdenum content was found in the Fe-Mo (50% Mo) deposits than in either the Co-Mo (40% Mo) or the Ni-Mo (20% Mo) deposits. The sodium citrate bath is an improvement over that proposed earlier (1) in that higher current efficiencies are obtained.

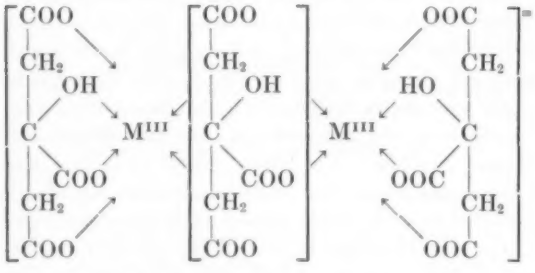
The results obtained can be explained by assuming

a series of reactions involving citrate and ammine complexes of the codepositing metals, and molybdate ions. Bobtelsky and Jordan (10) suggest the following structures for the citrate complexes of bivalent and trivalent metals:

(Structure I)
Bivalent metal citrate complex where molar ratio of citrate to metal ion is 1.0



(Structure II)
Trivalent metal citrate complex where molar ratio of citrate to metal ion is 1.5



Since nickel has the stable oxidation state of plus two, its complex would have structure I. Iron and cobalt, however, can have either plus two or plus three oxidation states and, therefore, an equilibrium mixture of structures I and II could be present.

By referring to Fig. 6 and 8, the following observations about the C.C.E. of the Co-Mo bath may be noted. In Fig. 6, as the molar ratio of citrate to metal ion decreases and approaches 1.0 (0.3 M/l metal sulfate) the C.C.E. of the bath increases, whereas at higher molar ratios (0.1 and 0.2 M/l metal sulfate), the C.C.E. curve is similar to the C.C.E. curve for the Fe-Mo bath. In Fig. 8, the C.C.E. of the Co-Mo bath decreases when the molar ratio of citrate ion to metal ion is between 0.6 and 1.0 (0.2 and 0.3 M/l Na_3Cit) and levels off when the molar ratio is greater than 1.0 (above 0.3 M/l Na_3Cit). It is possible that, at a molar ratio of citrate ion to cobalt ion of one, the citrate ion is capable of complexing Co(II) tightly enough to prevent the Co(III) ammine complex from forming when the solution is made ammoniacal. These observations could indicate that at the concentrations used the cobalt complex present in greatest amount has structure I. The fact that the C.C.E. for some Co-Mo baths is as high as the C.C.E. for some Ni-Mo baths is then to be expected since cobalt and nickel form the same type of bivalent metal citrate complex. If the trivalent metal complex were present to a larger extent, one would then expect the Co-Mo bath to behave more like the Fe-Mo bath. The following observations are made about the Fe-Mo bath from Figs. 6 and 8. In Fig. 6 the C.C.E. curve for the Fe-Mo bath starts to decrease when the mole ratio of citrate ion to metal ion is less than 1.5 (>0.2 M/l $FeSO_4 \cdot 7H_2O$) which may indicate that the structure I type of complex is being formed. In Fig. 8 the C.C.E. is constant up to a molar ratio of citrate ion to metal ion of 1.3 (0.4 M/l Na_3Cit) and when the molar ratio is 1.6 (0.5 M/l Na_3Cit) the C.C.E. curve starts to increase. These observations could indicate that a structure II complex for iron is involved. The fact that deposition occurs from highly ammoniacal solutions would make the bivalent complexes contain ammonia instead of water.

Assuming the above complex structures to be essentially correct, then for the deposition of the single metals (iron, cobalt or nickel) the following reactions may occur:

Metal citrate ammine ion $\rightleftharpoons$ Metal ammine ion
$+$ Citrate ion (I)

Metal ammine ion $\rightarrow$ Metal ammine-metal bridge (II)

Metal ammine-metal bridge $\xrightarrow[\text{exchange}]{\text{electron}}$ metal
$+$ ammonia (III)

All three metals are capable of forming the metal ammine complex; nickel and cobalt form stable ammines while the iron (II) ammine is rather unstable. It is assumed that for the iron and cobalt complexes there is an equilibrium between the two structures and that structure I can be formed from structure II by a dissociation mechanism and then structure I dissociates according to reaction (I). The metal ammine complex then migrates to the cathode and with the formation of a bridge complex, as postulated by Lyons (11), binds itself to the cathode and splits off ammonia. Deposition from the metal ammine ion can account for the C.C.E. observed. The nickel citrate ammine could easily split as in reaction (I) and would allow deposition to proceed at a greater rate than in the case of iron where the dissociation of the complex would be less, leaving little metal ammine ion from which deposition occurs. Therefore, the iron bath would be expected to operate at a lower C.C.E.

The fact that the percentages of nickel and cobalt in the deposit decrease when a series of deposits are made from the same bath without replenishing the metal ion concentration could indicate that reaction (I) is forced to the left due to common ion effect. The

main function of the citrate ion would be to keep the metal ion concentration low.

When molybdate is added, it does not necessarily have to be involved with the metal citrate ammine complex, but can retain its own identity as $MoO_4^=$ (the species most likely in an alkaline solution). Since the presence of iron, cobalt, or nickel is necessary to accomplish the reduction of molybdate to molybdenum [this would be reaction (IV)], these metals may be considered to be catalysts. Deposition of iron, cobalt, or nickel occurs as mentioned from the ammine complex, the $MoO_4^=$ may then be assumed capable of forming another bridge complex[4] with the cathode and be reduced. The actual reduction of the molybdate at the cathode may be accomplished by hydrogen. The black oxide that is present on some deposits may be due to partial reduction of the molybdate bridge complex.

The rate at which the molybdenum content increases in the three alloys may be explained as follows. If the competing reactions for the deposition process are considered to be reactions (II) and (IV), then reaction (II) depends upon the dissociation of the metal citrate ammine complex [reaction (I)]. There would be a greater concentration of nickel ammine than iron ammine and therefore a small amount of $MoO_4^=$ in the Fe-Mo bath will give a larger percentage of molybdenum than the same amount in the Ni-Mo bath simply because the molybdate ion has a better chance to come in contact with the cathode.

The fact that high concentrations of sodium molybdate decrease the C.C.E. of the bath can perhaps be explained in the following way. The $MoO_4^=$ can be considered to reach the cathode by diffusion, as postulated for the tungstate ion by Clark and Lietzke (12). When the $MoO_4^=$ concentration is high the cathode becomes covered with a thin insoluble film containing molybdenum in some oxidation state or states intermediate between the free metal and Mo(VI). This cathode film may prevent the metal ammine from which deposition of the catalytic metal occurs from reaching the cathode.

The detrimental effect of ammonium ion could be due to the instantaneous discharge of ammonium ion to ammonia and hydrogen in preference to the other cathode reactions.

Since the percentage of the codeposited metal in the alloy is increased with an increase in the bath temperature, it may be assumed that this is due to an increase in the dissociation of the metal citrate complex.

It is realized that the proof for this postulated mechanism is very scanty, but future work in this laboratory will be directed toward the investigation of the mechanism. It is quite probable that the process for the electrodeposition of tungsten alloys (13) from similar solution is much the same as the process involved in the electrodeposition of these molybdenum alloys.

[4] $MoO_4^=$ may be assumed capable of forming this bridge complex since it may have bonding orbits available in the 4*d* and 5 *s*, *p* levels.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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Periodic Current Reversal in Plating Copper-Lead Alloys[1]

NELSON W. HOVEY, JOHN L. GRIFFIN,[2] AND ALBERTINE KROHN

Chemistry Department, University of Toledo, Toledo, Ohio

ABSTRACT

Apparatus based on the commutator principle was designed and constructed to convert direct current to square-wave alternating current, and was applied in electrodepositing copper-lead alloys from a cyanide-tartrate solution. The procedure was successful in eliminating the nodules which occurred in alloy deposits obtained in previous studies using this type of bath.

INTRODUCTION

Previous studies of various methods of electroplating alloys of copper and lead reported that the most promising bath for this purpose was a cyanide-tartrate solution having the following composition (1, 2): NaOH—40.0 g/l; NaCN—147.0 g/l; $NaKC_4H_4O_6 \cdot 4H_2O$—211.7 g/l; CuCN—150.6 g/l; $Pb(C_2H_3O_2)_2 \cdot 3H_2O$—75.9 g/l. Using the operating conditions given in the experimental part of the earlier paper (but without current reversal), the alloy deposited from the freshly prepared solution contained approximately 70% copper. However, the deposits tended to be highly strained, brittle, and nodular. The work of Jernstedt (3) suggested the possibility of preventing the growth of nodules on deposits from this bath by the use of periodically reversed current.

The principal purpose of the research reported in this paper was to design and construct a simple, inexpensive device for converting direct current to square-wave alternating current of readily variable frequency and wave form. The limited work on copper-lead alloy plating using the apparatus described was done mainly to demonstrate that this method of producing periodic reversed current is practical. Data obtained were sufficient to show that nodule formation on deposits from this bath is inhibited by periodic current reversal.

No attempt was made to produce any particular alloy composition. The deposits obtained using periodic reversed current were higher in copper content than those produced with direct current under comparable conditions. Copper content increased as the percentage of anodic current was increased. Previous work (1) indicated that alloy composition may be varied within wide limits when direct current is used. It should be possible to compensate for the relatively faster dissolution of lead during the period that the deposit functions as the anode and produce deposits of any desired composition. That smooth bright deposits are obtainable over a wide composition range has not yet been proved.

The commutator principle appeared to furnish the method most likely to give an apparatus which was flexible but economical to build. Equipment characteristics thought desirable for this investigation include: (*a*) low-frequency limit of 10 cps; (*b*) the frequency variable over a range of five to ten times the lower limit; and (*c*) a means for varying the alternating current wave form to give variable ratios of plating to polishing current. Preliminary studies showed that nodule formation began early in the plating process. Nodules were discerned on several samples obtained after 30-sec plating time. To facilitate the action of the polishing fraction of the cycle in preventing or removing nodules, a minimum frequency of about 10 cps was chosen so that the polishing could start very early in the process.

CONSTRUCTION OF THE COMMUTATOR

Two 60-bar commutators from standard 24 volt generators were utilized. Fig. 1 shows the machined output commutator. Two series of 19 bars each were connected by soldering a heavy copper strap to the bars on the outer shoulder of each. The two resulting segments were separated by two series of 11 free bars each. Holes were drilled between each of the 22 free bars and between the last free bar and the end bar of the large segment. These holes were tapped for small machine screws. This arrangement was designed to permit the use of the machine screws as shorting plugs to permit the adjustment of the wave form by varying the connections between the free bars and the large segments.

The commutator produces two complete plating-polishing cycles per revolution. Since two cycles involve 60 bars, one bar is equivalent to $\frac{1}{30}$ or $3\frac{1}{3}$%

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[2] Present address: Chemistry Department, University of Michigan, Ann Arbor, Michigan.

of a cycle. Thus, the ratio of effective plating current is variable from 93⅓% to 20% of one cycle in steps of 6⅔%.

For example, suppose it is desired to have the plating current flow for 1/20 sec and the polishing current for 1/100 sec. The ratio of polishing current time to total cycle time is 1:6 or 16⅔%. The number of bars to be connected in the polishing current segment is then 16⅔ divided by 3⅓ or 5 bars.

To accomplish the required connection, the index bar in the polishing current section is connected to the following four free bars by inserting four of the brass screws. The hole between the fourth and fifth free bars is left open to isolate the polishing current segment from the plating current segment. The rest of the free bars are connected to the next large segment by inserting the rest of the screws. This procedure is repeated for the other side of the output commutator.

Fig. 2 shows the complete commutator and shaft assembly. The input commutator bars were connected by soldering a heavy copper strap to the outer end of each bar to form two segments of 30 bars each.

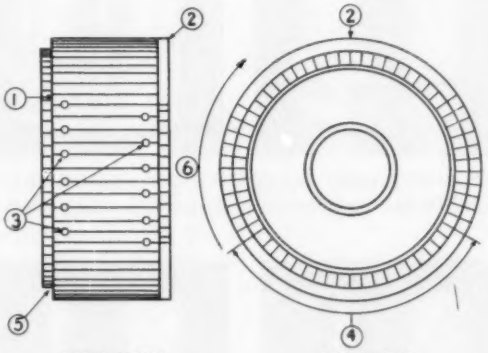

FIG. 1. Machined output commutator. 1—Index bar; 2—shorting strap; 3—holes tapped for machine screws; 4—large segment; 5—shoulder turned for connecting straps; 6—direction of rotation.

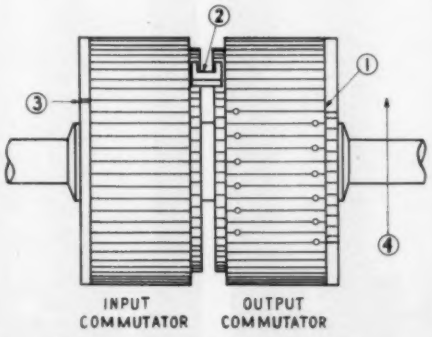

FIG. 2. Commutator and shaft assembly. 1—Index bar; 2—connecting strap; 3—segment separation point; 4—direction of rotation.

The separation points of these segments were positioned one bar ahead of the corresponding separation points on the output commutator. This resulted in a minimum polishing current fraction of 3⅓ of a cycle. Each input segment was then connected to the large output segment nearest it with heavy copper strap. No adjustment of the input commutator was needed since its connections were fixed.

A diagram of the brush holder assembly is shown in Fig. 3. The holder was constructed to present two

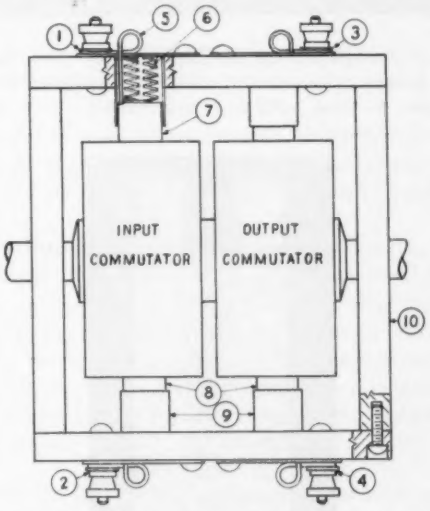

FIG. 3. Brush holder assembly. 1—D.C. plus input; 2—d.c. minus input; 3—a.c. to anode; 4—a.c. to cathode; 5—flexible lead to brush; 6—spring; 7—brush; 8—brushes; 9—holders; 10—Bakelite frame.

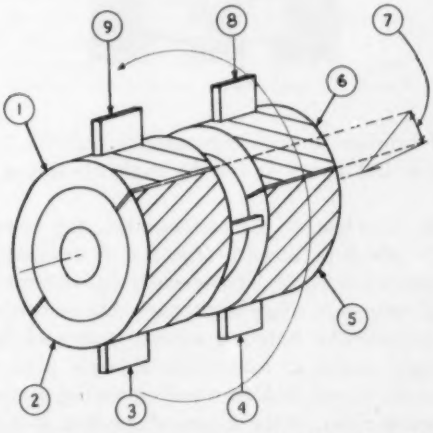

FIG. 4. Schematic representation of the principle of the commutator. 1—Input commutator segment, first half; 2—input commutator segment, second half; 3—input brush, d.c., negative; 4—output brush, a.c., to cathode; 5—output commutator segment, second half; 6—output commutator segment, first half; 7—angular separation of positions of polarity change in input and output commutators; 8—output brush, a.c., to anode; 9—input brush, d.c., positive.

FIG. 5. Complete commutator assembly. 1—⅓ hp electric motor; 2—commutators; 3—brush holder; 4—speed changer; 5—pivot bolt; 6—control handle.

FIG. 6. Typical deposit using direct current

fixed brushes to each commutator, normal to the surface, 180° apart, and under moderate spring pressure.

The principle of the commutator, the construction of which is shown in Fig. 1–3, is schematically represented in Fig. 4. The device is equivalent to two metal disks on a single shaft, each disk consisting of two semicircular halves insulated from each other. A single electrical connection extends from each semicircle of one disk to a corresponding semicircle of the other disk. If the sectors of one disk, instead of paralleling the sectors of the other disk, are rotated, then the geometrical arrangement is equivalent to that accomplished by changing the positions of the screws.

The commutator and shaft assembly was mounted in ball bearings which were attached to a base containing the brush holder, motor, and speed changer. The motor and speed changer drove the commutator shaft by means of V-pulleys and V-belts as shown in Fig. 5.

The frequency of alternation is changed by shifting the cone position of the speed changer. The control handle is moved toward the motor to decrease frequency and toward the commutator to increase

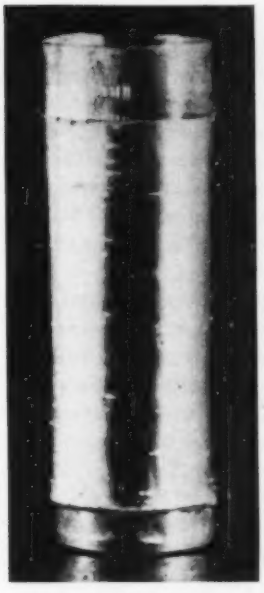

FIG. 7. Typical deposit with 10% anodic current.

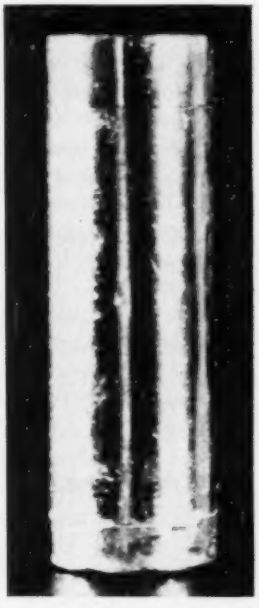

FIG. 8. Typical deposit with 20% anodic current.

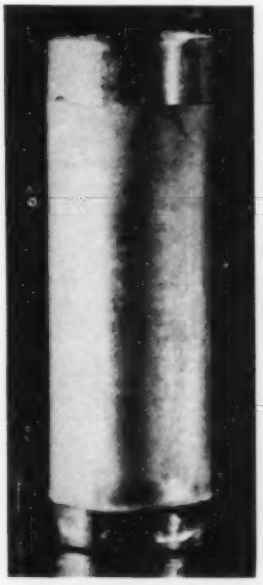

FIG. 9. Typical deposit with 30% anodic current.

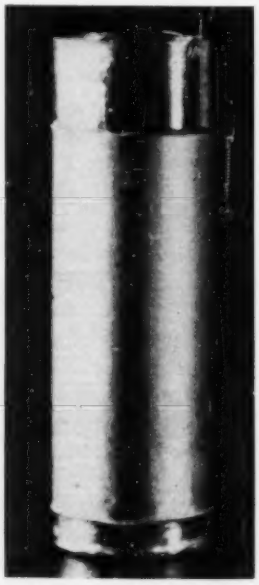

FIG. 10. Typical depcsit with 40% anodic current.

frequency. Once set, the handle is locked in place by tightening the wing nuts on the pivot bolts.

Experimental

Except for plating time, procedures and conditions used were the same as those found best in the earlier studies (1, 2). These were: temperature, 40°C; current density, 3.3 amp/dm² (30 amp/ft²); and cathode rotation of 1750 rpm. To compensate for the reduced effective plating time resulting from the use of alternating current, the total time was extended to equal 25 min of actual plating time for each run.

Results

The photographs of Fig. 6–10 show a typical series of deposits. The first (Fig. 6) is the extremely rough surface typical of a deposit using direct current. The nodules are dark gray, the background a dull, uneven copper color. This deposit was 57.6% copper.

The next series shows deposits made at a frequency of 30 cps with variations in the percentage of reverse current. Fig. 7 shows the deposit with 10% anodic current. The size and number of nodules have been reduced and the background is smooth. The deposit contained 60.3% copper.

The deposit when the current was 20% anodic is shown in Fig. 8. There are only a few rough spots; the rest is of high luster. Analysis showed 77.5% copper in the alloy.

With 30% anodic current, the deposit contained 93.6% copper and was free of nodules, but had only medium luster (Fig. 9).

Fig. 10, the deposit with 40% anodic current, is very smooth, of medium luster, and contains 98.8% copper.

Other runs made at 90 cps were similar in appearance and composition. Alloys deposited with anodic current values between 20–30% usually exhibited normal copper content and the most lustrous surfaces, while those deposited at high anodic current values showed a high copper content and smooth surfaces of medium luster.

Potential measurements indicated that polarization decreased with increasing percentages of anodic current, but no detailed study was made of this.

Conclusions

Very satisfactory apparatus for experimental work in electrodeposition using square-wave alternating current may be constructed at little cost.

Current reversal definitely reduces nodule formation on copper-lead alloy deposits from cyanide-tartrate solutions and makes it possible to obtain brighter deposits.

The deposits increase in copper content as the percentage of anodic current is increased. This indicates that lead is more active anodically than is copper in the cyanide-tartrate solution used. In order to compensate for this effect, either the solution must be modified or the plating conditions changed, or both, if relatively high lead content deposits are to be produced.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

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Graphite Anodes in Brine Electrolysis

III. Effect of Anode and Operating Variables on Caustic Color[1]

M. Janes,[2] N. J. Johnson, and E. B. Pilcher

Process Engineering Laboratory, National Carbon Company, A Division of Union Carbide and Carbon Corporation, Niagara Falls, New York

ABSTRACT

Caustic color data which have been obtained with a laboratory diaphragm chlor-alkali cell are summarized briefly. Effects of such cell operating variables as brine flow rate, brine concentration, and current density have been investigated. Measurements generally were made on the unevaporated catholyte effluent after addition of a reducing agent. The absorption spectrum appears identical with that of the compound isolated and identified by Heller. Light absorption by this pyromellitic acid chlor-quinol obeys Beer's law, so that degree of cell effluent coloration can be expressed in terms of the concentration of this compound. Chemical oxidation of graphite, as by hypochlorous acid, is believed to be an important factor in formation of the color-producing compound. As is known, caustic color is much less with treated graphite, consistent with the protection thus obtained against internal attack.

Introduction

The appearance of a blue or purple color in 50% caustic produced by evaporating the cell effluent from diaphragm chlor-alkali cells equipped with graphite anodes has long been familiar (1). Heller's work (2) demonstrated that the color was due to an organic compound derived from oxidation of the graphite anodes. By extraction of used graphite stubs with water and subsequent purification of the extract a yellow crystalline compound was isolated which, when dissolved in caustic solution, would reproduce all the usual colors met in plant operation. Analytical and physicochemical studies of this compound led Heller to suggest a pyromellitic acid chlor-quinol structure.

As Heller noted (2), Cushing studied the caustic colors spectrophotometrically and found that a blue caustic solution prepared from the yellow compound isolated by Heller has the same spectral transmission curve as plant liquor.

Measurements of the degree of coloration as affected by variations in graphite or such cell operating conditions as temperature, brine concentration, etc., have been carried out in this laboratory during the past 13 years, employing a laboratory diaphragm cell. These measurements are fully in accord with Heller's conclusions and show the variation of concentration of colored compound with cell operating conditions and type of anode material.

Experimental

The laboratory diaphragm chlor-alkali cell in which these studies were made has been described (3). Unless otherwise stated, data presented here are for laboratory cell operation at 11 amp (approx. 0.5 amp/in.^{2} anode current density), feed rate of 200 ml/hr saturated NaCl solution, and 80°C.

Color measurements were made directly on the cell effluent, with a reducing agent added to bring the light absorption by the color compound into the visual spectrum. Heller noted that a red or pink color develops if hot, unconcentrated cell effluent is treated with reducing agents such as dextrose, etc., and that the intensity of the red color seems to be an indication of the quantity of the coloring matter present. Sodium dithionite (hydrosulfite) at room temperature was used here.[3] In the earliest work, the intensity of color developed was estimated visually in Nessler tubes, later with a photoelectric colorimeter, and recently with a Beckman Model "B" spectrophotometer. Fig. 1 shows the transmission curve of effluent from an operating laboratory diaphragm cell compared to a solution of the compound isolated by Heller[4] in a synthetic medium of essentially the same composition as that of cell effluent (81 g/l NaOH, 223 g/l NaCl). Values of log A_s are plotted against wave length of light from 380 to 620 mμ.[5] The close correspondence of the two

[1] Manuscript received September 13, 1954. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

[2] Present address: National Carbon Research Laboratories, Cleveland, Ohio.

[3] Suggested by Howard Wells of Niagara Alkali Company.

[4] Samples of this compound were kindly supplied to the authors by Heller.

[5] The terminology and symbols for absorbancy (frequently called optical density) follow the recommendations of Mellon (4). The advantages of a log A_s plot are described by Stearns (5).

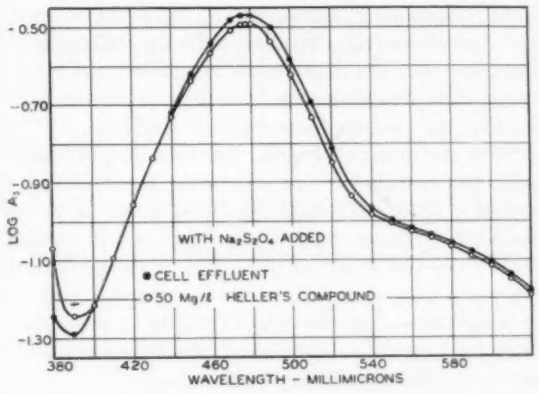

FIG. 1. Comparison of the absorption curve of laboratory cell catholyte with that of Heller's compound in alkaline chloride medium (with dithionite added).

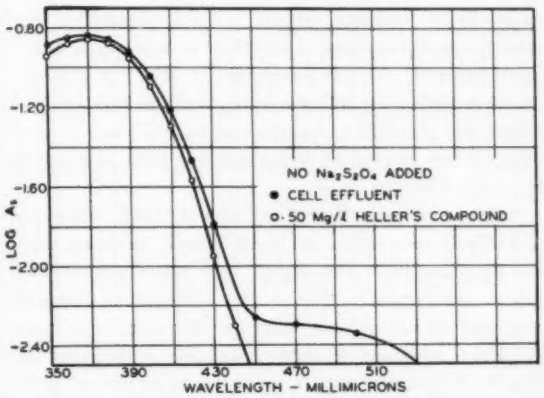

FIG. 2. Comparison of the absorption curve of laboratory cell catholyte with that of Heller's compound in alkaline chloride medium (no reducing agent added).

curves is strong evidence that the compound isolated by Heller is responsible for the color thus developed in cell effluent. There is a maximum absorption at 480 mμ; but it is interesting that on adding $Na_2S_2O_4$ and gently agitating, a cherry red color appears initially which quickly changes to a reddish-brown. This change in color is so rapid that it has not been possible to obtain a transmission curve of the transient reduction product. The difference in absorption below 400 mμ indicated in Fig. 1 is no doubt due to slight differences in $Na_2S_2O_4$ concentration, which absorbs below this wave length.

In Fig. 2, the same cell effluent is compared with the same synthetic solution without addition of reducing agent. Again the curves correspond quite closely, with a maximum (in the spectral region shown) at about 372.5 mμ, possibly corresponding to the maximum observed by Heller for the compound in absolute alcohol solution at 350 mμ.

Fig. 3 shows that the absorption of Heller's compound at 480 mμ (after treatment with $Na_2S_2O_4$) follows Beer's law quite closely, i.e., the absorbancy is linear with respect to concentration. This relation has been used to convert the authors' absorption measurements to concentration of color compound.

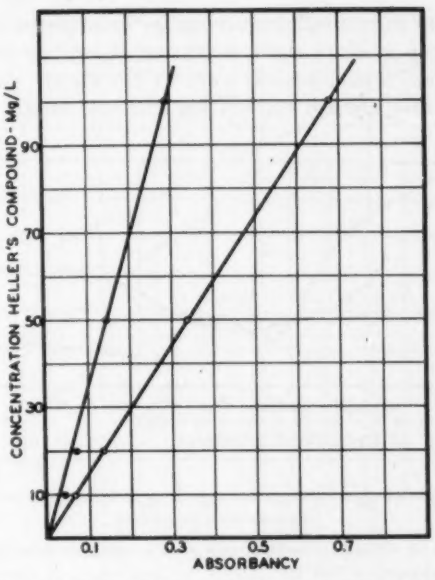

FIG. 3. Concentration of Heller's compound vs. absorbancy. ○ At 480 mμ with dithionite added; ● at 372.5 mμ without dithionite.

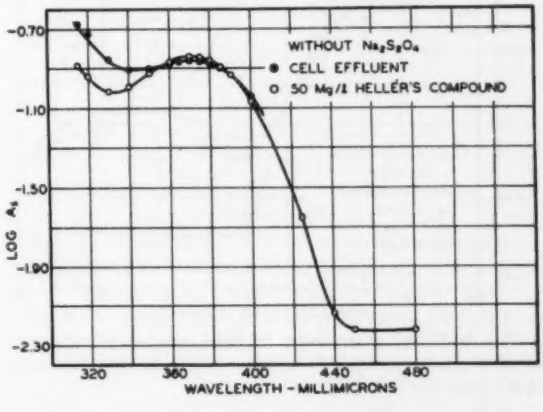

FIG. 4. Comparison of absorption of laboratory cell catholyte with that of Heller's compound in alkaline chloride medium at shorter wave lengths (no dithionite added).

The upper curve of Fig. 3 indicates that the absorption maximum at 372.5 mμ without treatment with a reducing agent does not follow Beer's law as well, and the measurement is less sensitive.

With an ultraviolet spectrophotometer, it is quite probable that equal sensitivity could be achieved without adding the reducing agent. As shown in Fig.

4, both the cell effluent and Heller's compound in an alkaline medium show increasing absorption below 330 mμ. Measurements down to 315 mμ are shown, but these are not too reliable with the Model "B" spectrophotometer (glass prism), requiring a very wide slit opening. Studies with an ultraviolet spectrophotometer might reveal the presence of other compounds similar to that isolated by Heller, but without the chromophoric quinone structure.

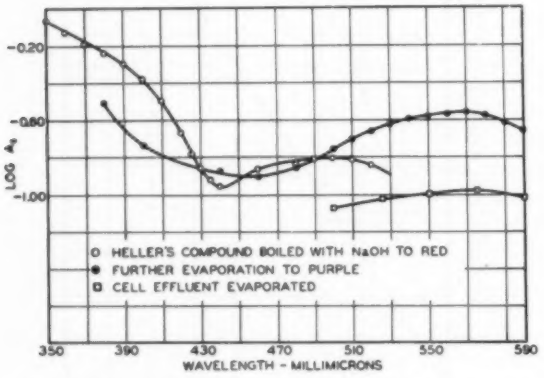

FIG. 5. Changes in absorption as a result of heating in the presence of NaOH.

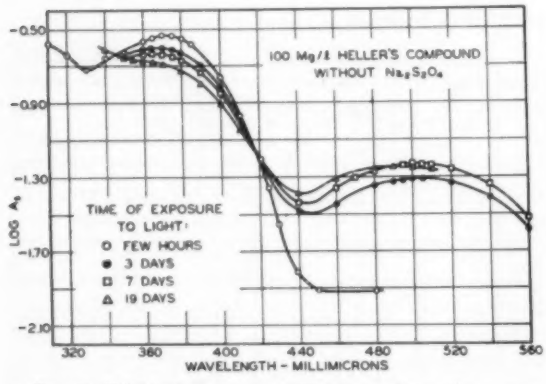

FIG. 6. Effect of exposure to light on absorption curve of Heller's compound in alkaline solution (no reducing agent added).

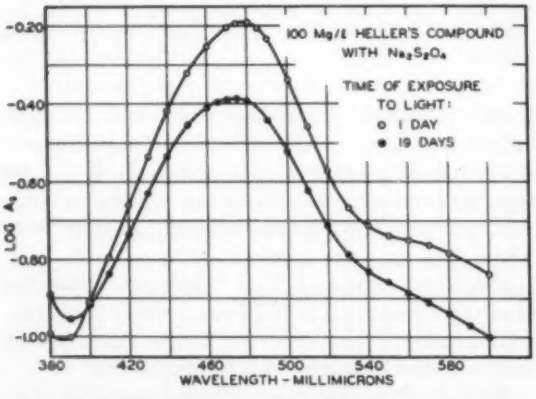

FIG. 7. Effect of exposure to light on absorption curve of Heller's compound in alkaline solution. Dithionite was added just prior to each series of measurements.

With the ultraviolet spectrophotometer not available, use of dithionite as a reducing agent and absorbancy measurements in the visual range was most convenient. Measurements should be made within 20 to 30 min after adding dithionite, since significant decreases in absorption have been observed after 2 or more hours. The cell effluent should be protected from light prior to addition of the reducing agent and performing the measurements.

Heller reported that the compound he isolated, when boiled with NaOH, behaves just as does cell effluent, developing a blue or purple color believed to be associated with the replacement of the chlorine atom by a hydroxyl group. Fig. 5 illustrates the changes in absorption. The effect of moderate heating appears to be the development of a flat absorption band at about 500 mμ (red); with further evaporation an absorption band at about 575 mμ is evident. Even moderate heating eliminates the peak at about 370 mμ.

Samples of cell effluent and of a synthetic solution of Heller's compound in NaOH-NaCl medium turn red on exposure to sunlight. This phenomenon was noted previously by Heller (2). Changes in the absorption spectrum for various times of exposure (without addition of dithionite) are illustrated in Fig. 6. A broad absorption band was observed with a flat maximum at about 500 mμ accompanied by a decrease in absorption at 370 mμ. The maximum at this latter wave length shifts slightly to shorter wave lengths and, after 19 days, the valley below 360 mμ has essentially disappeared. The changes produced in the absorption spectrum by exposure to light appear similar to those produced by mild heating.

The effect of exposure to light on the absorption spectrum with reducing agent added is illustrated in Fig. 7. The general form is little changed, but the absorption peak is considerably reduced and shifted slightly (to about 475 mμ). If absorption at 480 mμ is characteristic of one form of the color compound,

TABLE I. *Effect of standing exposed to light of a solution of 100 mg/l of the color compound in alkaline medium*

Time in days	$Na_2S_2O_4$ added	
	A_s at 480	mg/l
0	0.680	100
1	0.642	95
3	0.573	84.5
7	0.524	77.5
19	0.411	61

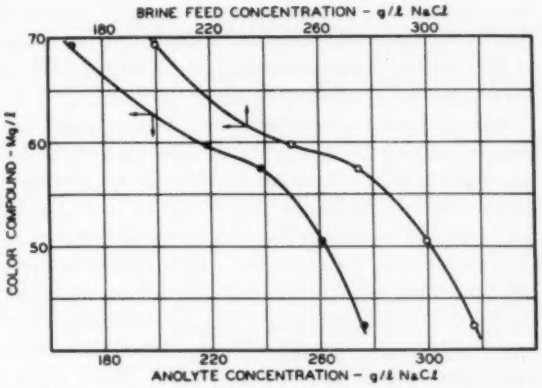

FIG. 8. Effect of anolyte chloride concentration on intensity of caustic color.

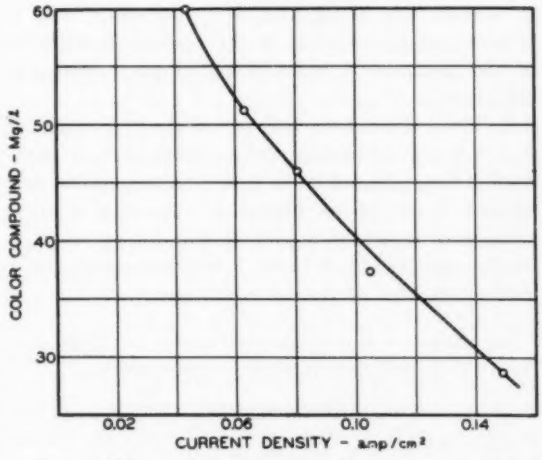

FIG. 9. Effect of anode current density on intensity of caustic color.

the decrease in concentration with time can be established (see Table I).

It is presumed that the apparent decrease in concentration represents not destruction, but transformation to another form which does not absorb at 480 mμ.

From Fig. 3, absorption can be expressed in terms of concentration of color compound. This same procedure was employed for certain of the older determinations made with a less selective photoelectric colorimeter, employing a plot of per cent transmission against concentration of the color compound in NaOH-NaCl medium. With the older instrument, Beer's law was not followed, because of the broad band of wave lengths of light used.

DISCUSSION

Laboratory diaphragm cell studies have confirmed Heller's conclusion that the color compound is produced by oxidation of the graphite as indicated by the following observations.

1. With a nongraphitic anode such as platinum, no color is produced. This eliminates other cell materials as a possible source of color.

2. Spectroscopic purification of graphite does not decrease the amount of color compound produced, indicating that impurities in the graphite are not responsible.

3. Color intensity has been found in general to increase with increased rate of attack on the graphite.

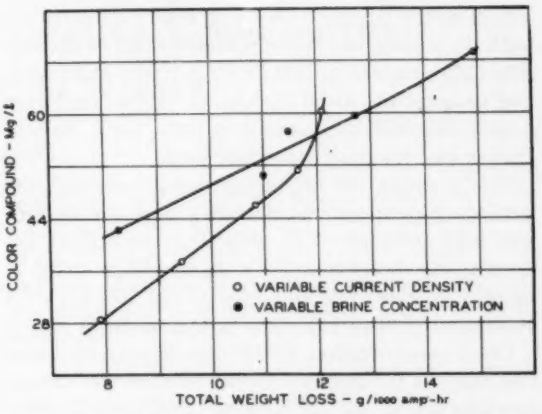

FIG. 10. Relation of intensity of caustic color to rate of anode attack.

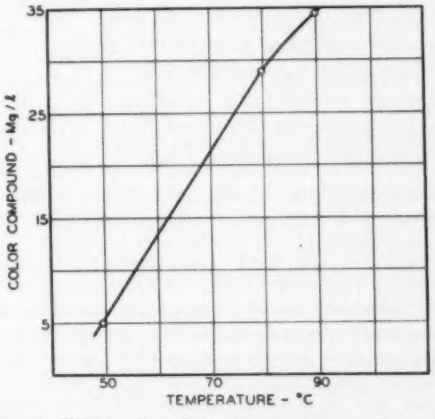

FIG. 11. Effect of anolyte temperature on intensity of caustic color.

TABLE II. *Comparison of anodes processed from various raw materials*

	Total weight loss G/KAH	Color compound mg/l
Standard graphite-high density..	6.41	25
Pregraphitized coal.....	7.88	36
Lignin.....	6.80	40
Lampblack.....	9.90	47
Charcoal.....	8.94	50

Fig. 8 illustrates the increase in color concentration with decreasing brine feed concentration, with feed rate held constant at 200 ml/hr, current at 11 amp, and temperature at 80°C. The curve for color compound concentration against anolyte NaCl concentration has essentially the same form.

Fig. 9 shows the increase in color concentration with decreasing current density.[6] Here the current was held constant at 11 amp, but the size of the anodes was varied from $\frac{5}{8} \times \frac{5}{8} \times 1\frac{1}{2}$ in. to $\frac{7}{8} \times \frac{7}{8} \times 4$ in. Feed rate was constant at 200 ml/hr of concentrated brine and temperature at 80°C.

Color concentration in the cell effluent for these two series is plotted against the total weight loss of graphite in Fig. 10. The general trend in both series for an increase in color concentration with increased rate of graphite attack is clearly evident. Cell temperature has quite a marked effect on color concentration, corresponding to an equally marked effect on rate of anode attack (see Fig. 11).

There is considerable evidence that chemical oxidation may be an important factor in the production of the color compound. Thus, the compound has been produced by oxidation of graphite particles with a hypochlorite solution without current, the reddish-brown color developing on addition of alkali and dithionite to the supernatant solution.

The increased graphite attack with decreasing current density is believed to be associated with an increased amount of chemical oxidation as discussed previously (6). However, the evidence is certainly not sufficient to permit the statement that chemical oxidation is solely responsible, and a similar colored compound has been found to be formed when graphite is employed as anode in a sodium carbonate electrolyte. It would be difficult to explain the color formation in such an electrolyte by chemical oxidation alone.

With treated graphite, color concentration in the cell effluent is markedly lower, of the order of 5 mg/l as compared to 40 mg/l for untreated stock. This is believed largely a result of the protection afforded by the treatment against internal attack (chemical oxidation).

Table II shows that the use of less graphitic raw materials for the anode, such as lampblack or charcoal, gives increased color concentration in the cell effluent. It can be speculated that the smaller crystallite size results in a greater exposure of surface for the specialized mode of oxidation which leads to the formation of the color compound.

[6] These data show the effect of current density on the concentration of color compound in the catholyte effluent with composition of the anolyte and catholyte (with respect to NaOH and NaCl concentration) held constant. From the definition of current density (amperes per unit area) a decrease in current density means an increase in graphite area exposed to the anolyte per unit of current. If the alternative procedure of maintaining constant area of graphite and varying the current is employed, it is necessary that the feed rate be varied in direct proportion to the change in current, in order to maintain a constant composition of anolyte and catholyte. If current is increased, with less than a proportional increase in flow rate, the NaCl concentration of the anolyte will be decreased and more migration and diffusion of hydroxyl ions from catholyte to anolyte will occur. The effect of such changes in the anolyte on the production of color compound could readily mask the effect of a decreased area of graphite per unit of current.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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The Influence of a Surface Active Agent on the Electropolishing of Copper[1]

K. F. Lorking

Corrosion Group, Aeronautical Research Laboratories, Department of Supply, Melbourne, Australia

ABSTRACT

Previous work has shown that surface active agents can improve the finish obtained on copper electropolished in orthophosphoric acid solutions, and this beneficial action is examined in greater detail. The evidence indicates that the cationic surface active agent cetyl trimethyl ammonium bromide is adsorbed at both the anode surface and on the walls of oxygen bubbles. These factors are shown to account for the improvement in the micropolishing characteristics of the bath and in the reduction in the size of the pits formed on the anode during slow oxygen evolution.

Introduction

Research on the use of surface active agents in electropolishing baths was reported by Sparks (1) who showed that the presence of such agents could increase the "throwing power" of the bath. This work was confirmed by Tajuna and Mori (2) during experiments on the electropolishing of nickel. More recent work (3) has shown that the addition of the correct concentration of certain surface active agents improves the finish of the region of medium current density polishing produced on copper anodes in orthophosphoric acid solutions. The main effects are:

(*A*) The "throwing power" of the bath, i.e., the ability to produce continuous polishing over an anode placed at an acute angle to the cathode, is increased.

(*B*) The reflectivity of the polished surface is increased.

(*C*) The size of the surface mounds, produced as slow oxygen evolution commences, is greatly decreased.

These factors produce a general improvement in the electropolished surface, and the present paper describes work undertaken to determine the mechanism by which this occurs. Experiments were carried out on copper in orthophosphoric acid solutions, and the surface active agent chosen for examination was cetyl trimethyl ammonium bromide (subsequently referred to as C.T.A.B.) which was available in purified form, and which was known to improve the finish obtained on copper anodes (3).

Experimental Method

It is known (4, 5, 8, 9) that the anodic surface finish obtained in an electropolishing bath depends on the characteristics of the anode layer and the anode surface film. Hence, the first step in determining the mechanism of the improvement produced in electropolishing by surface active agents was to determine whether such agents were adsorbed on the anode surface. This was investigated by the following three methods: (*a*) by observing the influence of increasing concentration of surface active agent on the finishes obtained on plates from Hull cell tests; (*b*) by measuring and comparing anode potential-current density relationships in solutions of gradually increasing concentration of surface active agent; and (*c*) by measuring the contact angles between the anode and a series of freshly blown bubbles pressed onto the surface. Such measurements were made for a number of values of the cell current between zero and that causing rapid oxygen evolution.

An important influence of suitable surface active agents in electropolishing solutions is to decrease the size of the mounds produced on the anode surface during oxygen evolution. These mounds have been shown (6) to be due to oxygen bubbles remaining for a significant period on the anode surface. Direct experimental investigation of the effect of surface active agents on the behavior of bubbles formed on the anode surface is difficult, so the following indirect methods were used.

(*A*) The effect of concentration of surface active agent on the surface tension of orthophosphoric acid was determined in an attempt to indicate the concentration of surface active agent at which significant adsorption occurred on oxygen bubbles.

(*B*) The effect of ageing a bubble in the solution on the contact angle between bubble and anode surface was determined.

(*C*) The effect of concentration of surface active agent on the size and speed of release of oxygen bubbles formed on the anode surface was determined qualitatively.

The solutions used in this work consisted of ortho-

[1] Manuscript received July 16, 1954.

phosphoric acid containing gradually increasing concentrations of C.T.A.B., prepared in the following way. A large quantity of orthophosphoric acid solution containing 581.9 g/l orthophosphoric acid was made up from May and Baker's orthophosphoric acid (sp gr 1.75) and distilled water, using a Griffin and Tatlock hydrometer to determine when the required specific gravity of 1.293 had been reached. A solution was then prepared containing 10 g/l C.T.A.B. (produced from cetyl alcohol purified by fractional distillation) in orthophosphoric acid. Solutions of orthophosphoric acid containing the required amounts of the surface active agent could then be prepared.

Experimental Results

Adsorption of Surface Active Agents at Anode

(*a*) *Hull cell experiments.*—Experimental verification was first made of the fact that C.T.A.B. produces a beneficial effect on the electropolishing of copper in orthophosphoric acid solution. Hull cell experiments showed that the electropolished surface was improved, and the "throwing power" of the bath was increased, by the addition of surface active agent over the range of concentration 0.002–0.005 g/l. At concentrations smaller than 0.002 g/l, mounds were produced at the commencement of slow oxygen evolution, and this effect reappeared and became more pronounced in the concentration range 0.005–0.1 g/l of surface active agent. Higher current densities at the latter concentrations resulting in rapid oxygen evolution caused the formation of furrows in the specimen surface. These effects are shown diagrammatically in Fig. 1 and 6. The diagrams show the appearance of the immersed sections of "Hull" cell plates after being used as anodes in the phosphoric acid solutions.

(*b*) *Measurement of anode potential-current density relationships.*—The apparatus used consisted of two copper electrodes in a cubic glass cell 1½ in. high. The 1 in. x 1 in. anode rested on the bottom of the cell and the 1⅜ in. x 1⅜ in. cathode was fixed horizontally at a distance of ¾ in. from the anode. Copper wire leads were welded to the electrodes and covered with several coats of lacquer. Current was supplied to the cell from a 6 v accumulator and regulated by suitable controls. The tubulus of the reference electrode projected through a hole in the center of the cathode so that the open end was within ⅛ in. of the anode surface.

The anode was subjected to an anodic current of 1 amp/in.² in orthophosphoric acid before each experiment. This standard treatment was necessary, as it was found that the anode potential-current density

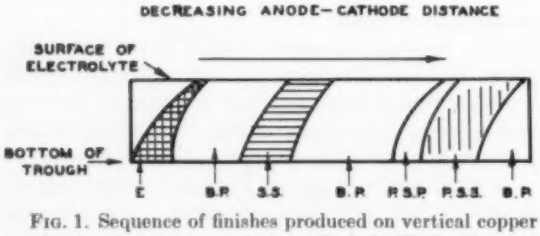

Fig. 1. Sequence of finishes produced on vertical copper anode placed at acute angle to cathode in Hull cell, using orthophosphoric acid electrolyte. The voltage across the cell was 6 v, the current 3 amp, and the average current density 1.5 amp/in.². E—electroetched surface; B.P.—bright polish; S.S.—smooth surface; P.S.P.—polished surface, pitted by slow oxygen bubble evolution; P.S.S.—polished surface, streaked by bubbles; P.S.H.S.—polished surface, heavily streaked.

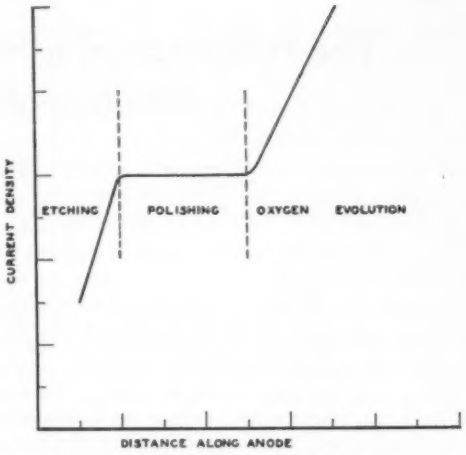

Fig. 2. Diagram showing current density distribution along Hull cell. The form of this graph was calculated by measuring the anode potentials corresponding to the various finishes while the cell was working, and determining the current densities corresponding to these potentials from current density-anode potential relationships determined for copper in an identical electrolyte.

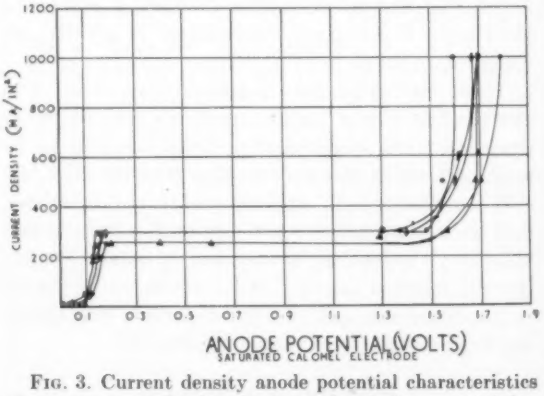

Fig. 3. Current density anode potential characteristics of copper in orthophosphoric acid solutions containing various C.T.A.B. concentrations. ●—581.9 g/l orthophosphoric acid; △—581.9 g/l orthophosphoric acid with 0.001 g/l C.T.A.B.; □—581.9 g/l orthophosphoric acid 0.005 g/l C.T.A.B.; ◇—581.9 g/l orthophosphoric acid with 0.01 g/l C.T.A.B.; ○—581.9 g/l orthophosphoric acid with 0.1 g/l C.T.A.B.

relationship over the entire range of potentials was dependent on the initial state of the surface. The effect of surface active agent on the anode potential-current density relationship is shown in Fig. 3. The addition of as little as 0.001 g/l of C.T.A.B. decreased the potential corresponding to oxygen evolution. This effect tended to become more marked as the concentration of surface active agent was increased, indicating that the oxygen overvoltage on copper in orthophosphoric acid is decreased by the presence of surface active agent.

(*c*) *Measurements of contact angles of bubbles on anode surfaces.*—These experiments were made in an apparatus based on that devised by Taggart, Taylor, and Ince (7) for the measurement of contact angles on mineral surfaces for flotation studies. The electrolytic cell was the same as that described in the previous section except that a hole was drilled through the cathode so that a glass capillary, through which air could be bubbled, could be brought near the anode. The cell rested on an adjustable platform attached to a vertical stand immediately to the left of the camera, and the magnified image of the anode surface, air bubble, and the end of the capillary could be focussed on the ground glass screen at the rear of the camera (see Fig. 4). The contact angle between the bubble and the anode surface was measured from this image, using a transparent protractor, after tapping the cell to insure that the equilibrium angle was obtained.

The results are given in Table I. It is necessary to emphasize that it is impossible to measure accurately contact angles of less than 10°, and such angles could only be reported as "small."

At cell voltages below 1.5 v, etching took place; at higher voltages polishing occurred.

It was found that, as the concentration of surface active agent was increased, it was often impossible to make contact using bubbles which had "aged" in solution for short periods, viz., 30 sec, so that it was necessary to blow the bubble directly onto the anode surface.

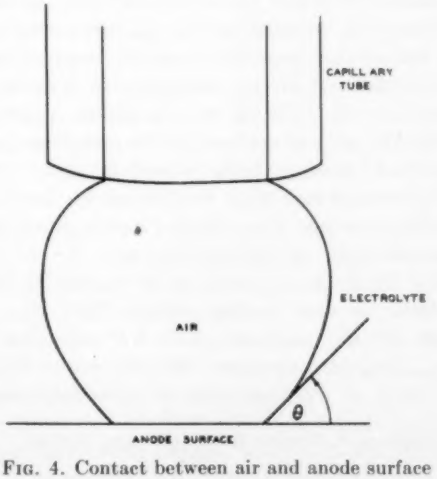

FIG. 4. Contact between air and anode surface

TABLE I. *Effect of C.T.A.B. concentration on contact angle*

Concentration of C.T.A.B. (g/l)	Current density (ma/in.²)	Cell voltage (v)	Contact angle
0	200	1.3	0
	232	1.2	0 No tendency for bubbles
	266	2.0	0 to adhere to anode sur-
	286	2.5	0 face
	294	2.5	0
0.001	0	0	20°
	200	1.4–1.7	0
	200	2.4	0
	200	2.6	0
0.002	0	0	50°
	135	1.3	25°
	150	1.4	10°
	160	2.6	Small
0.0025	0	0	65°
	150	1.5	10°
	200	2.0–2.3	Small
	200	2.6	Small
0.003	0	0	10°
	200	1.2	Small
	225	1.2	Small
	300	1.6	Small
	330	2.2–2.5	10°

The results given in Table I indicated that surface active agent was adsorbed onto the copper surface and remained adsorbed up to quite high anode potentials. Further experiments showed that the surface active agent could remain adsorbed on the anode surface while polishing was proceeding, i.e., at cell voltage above 1.5 v (see Table II), but was gradually desorbed. It is possible that the positively charged C.T.A.B. ions were repelled from the anode surface, also that the cupric ions formed complex ions with the C.T.A.B. ions, which are substituted ammonium ions. Renewal of the solution or agitating the anode caused further adsorption of surface active agent.

Effect of a Surface Active Agent on Bubble Formation and Release

Surface tension measurements.—A determination was made of the effect of C.T.A.B. on the surface tension of orthophosphoric acid. The measurements were made by means of a Du Noüy tensiometer with a platinum ring. All glassware and the ring were cleaned with hot chromic acid and thoroughly washed with distilled water before making measurements. It was found that the surface tension values for the C.T.A.B. solutions decreased slowly, indi-

TABLE II. *Change of contact angle with time*

Current density was 300 ma/in.[2] and the solution contained 0.01 g/l C.T.A.B.

Time (sec)	Voltage (v)	Contact angle
30	1.3	40
90	1.5	40
150	1.6	40
210	—	Small
270	2.5	50
330	2.5	Small
390	2.5	Small

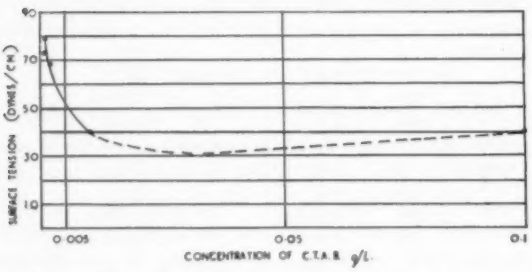

FIG. 5. Effect of C.T.A.B. concentration on the surface tension of orthophosphoric acid solution.

cating a slow increase of adsorption of C.T.A.B. at the interface. For example, when the C.T.A.B. concentration was 0.002 g/l the surface tension decreased from 70 to 62 dynes/cm in 10 min. Readings were therefore taken over a period of 10 min at 2-min intervals, and the mean result taken. With higher C.T.A.B. concentrations this effect was much less pronounced. This increasing adsorption of C.T.A.B. at the air-water interface was also noted during the contact angle measurements. Results are presented in Fig. 5 and show that the critical concentration (i.e., that corresponding to micelle formation) of C.T.A.B. in orthophosphoric acid is 0.01 g/l.

Influence of bubble "age" and concentration of surface active agent on the contact angle formed by a bubble pressed on the anode surface.—If a bubble was kept "ageing" in the solution for a period before being pressed against the anode surface, or if the concentration of C.T.A.B. in the solution was increased, then the amount of adsorption of surface active agent on the bubble wall was increased, and it became more difficult to make contact between the bubble and the anode surface. When the concentration of C.T.A.B. reached 0.003 g/l the rate of adsorption on the bubble was rapid, and it became more difficult to make bubble to anode contact.

Influence of surface active agent on bubble release.—It was noted that only very small oxygen bubbles were present on the anode surface with 0.001–0.005 g/l C.T.A.B. in the electrolyte, and these were rising freely from the anode surface.

Further Hull cell experiments.—A series of tests carried out with a surface active agent containing two ammine groups[2] showed that the effects of alterations in the concentration of this addition agent were very similar to those noted with C.T.A.B. Optimum electropolishing was obtained at the critical concentration (0.01 g/l) in the orthophosphoric acid bath.

When amyl xanthate was studied, it was found that at relatively high concentrations ($\geqslant$0.05 g/l) xanthate was adsorbed on the anode surface and subsequently oxidized to form a yellow film (probably consisting of dixanthogene) which partially passivated the electrode surface. Unfilmed areas were electropolished. Using 0.0025 g/l of xanthate the same sequence of finishes was obtained as in the absence of the xanthate, but the quality of the electropolishing was significantly improved.

Discussion

The experiments described in this paper show that addition of the correct quantity of C.T.A.B. to orthophosphoric acid solutions used as electrolytes for electropolishing copper has two main effects on the anodic finish obtained. First, a brighter polish was obtained, and second, the size of the mounds produced on the anode surface during slow oxygen evolution were reduced in size and number, giving an effective increase to the throwing power of the bath when using medium current density polishing.

The results of contact angle measurements showed that surface active agent was adsorbed on the copper surfaces before current was passed across the cell, and that significant quantities of the surface active agent remained adsorbed on the surface for a significant period while current was passing across the surface.

Results of other work indicate that as oxygen bubbles were formed on the anode surfaces, adsorption of surface active material occurred on the bubble walls. It is now necessary to consider how adsorption of C.T.A.B. on the anode surface and adsorption of the surface active agent on bubble walls could produce better anodic finishes.

It is considered (4, 5, 8, 9) that, in the electropolishing process, the polishing action is set up by an anode layer and an anodic film.

The anode layer is a layer of electrolyte, whose thickness is considerably greater than the wave length of the electrode profile for successful electropolishing to take place (10). The anode film is a thin layer of solid material or adsorbed atoms or

[2] Duomeen S, Armour & Co., Chicago, Illinois.

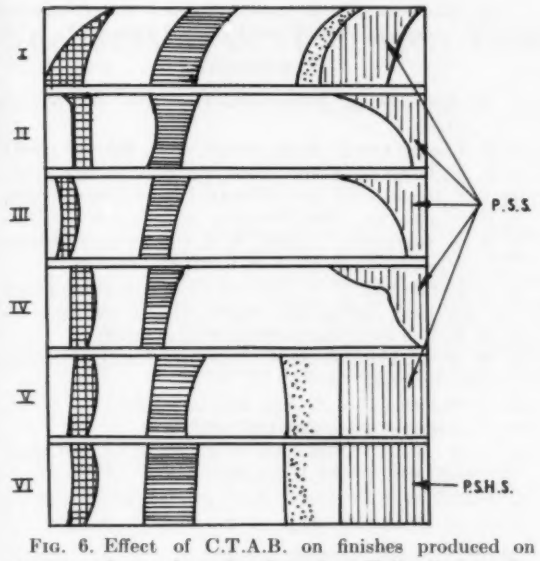

FIG. 6. Effect of C.T.A.B. on finishes produced on copper anodes, as shown by plates from Hull cell tests. I—581.9 g/l orthophosphoric acid; II—same as I with 0.001 g/l C.T.A.B.; III—same as I with 0.002 g/l C.T.A.B.; IV—same as I with 0.005 g/l C.T.A.B.; V—same as I with 0.01 g/l C.T.A.B.; VI—same as I with 0.1 g/l C.T.A.B.

molecules (4, 5). The polishing action is considered (8–11) to be due to a diffusion-controlled anodic solution process being set up through the anode layer and film.

It is thought probable that adsorption of surface active agent on and close to the anode surface could help to control ion diffusion processes in two ways: by mechanical blocking, and by replacement of water molecules in this region. The latter process may affect the dielectric constant of the medium and lower the number of water molecules available for solvating cations, hence lower the rate of diffusion of cations away from the anode surface.

The next question to be discussed is the influence of adsorption of C.T.A.B. on bubbles formed on anode surfaces during electropolishing. It has been found (6) that the protuberances surrounded by depressions which form on the anode surface are due to oxygen remaining on the surface for a period, there influencing the rate of anodic solution. The present work shows that adsorption of C.T.A.B. takes place on the bubble walls and this would be expected to accelerate the removal, by its bouyancy, of the bubble, due to the lowering of the surface tension at the air water interface by C.T.A.B. adsorption. [The force necessary to remove a bubble from contact with a solid surface is (12) $T(1 - \cos \theta)$, where T is the surface tension of the liquid, and θ is the equilibrium contact angle.]

The effect of high C.T.A.B. concentrations is to increase adhesion of oxygen bubbles to the surface, as indicated by results shown in Fig. 6. When the C.T.A.B. concentration is increased to 0.01 g/l, bubbles formed as slow oxygen evolution commences adhere sufficiently long to cause pitting; if the concentration is increased to 0.1 g/l, the pitting is more evident, and the bubbles cling to vertical bubble-paths and produce deep grooves by preventing adequate anode layer formation.

Therefore, when the concentration of surface active agent becomes high enough, i.e., $\geqslant$ 0.01 g/l, for a significant quantity to remain on the anode surface at anode potentials positive enough to cause oxygen evolution, then the adhesion of the bubbles to the anode surface will become greater than in the absence of surface active agent. This change is due to the contact angle of the bubble formed on the anode surface increasing as the surface becomes more paraffinic in nature. Such a change is not indicated by contact angle measurements as the test bubble armored too rapidly for ready contact.

Finally, it is necessary to discuss the choice of the correct type of surface active agent to add to a polishing bath for a particular metal. In order to improve the surface finish obtained in aqueous electropolishing baths, there are two main objectives, as set out in the following paragraphs.

To reduce the size and number of mounds formed during oxygen evolution, it is considered that the addition of the critical concentration of the majority of long chain surface active agents will achieve this effect by causing the early release of oxygen bubbles from the anode surface.

To decrease the micro-irregularities and increase the brilliance of the finish, it is considered that it is necessary to achieve uniform formation and diffusion of cations from the anode surface, on a microscale. It is probable that addition of the critical concentration of the correct type of surface active agent contributes to this control, at least for the system copper in phosphoric acid. It is difficult to indicate which surface active agent will give satisfactory results. A surface active sulfate (3), ammine, and diammine, also potassium amyl xanthate have been shown to improve the electropolished surface obtained on copper in orthophosphoric acid.

The results obtained using xanthate also indicate that this agent was adsorbed on the anode surface, and substantiate the theory that adsorption of organic ions on or at the anode surface during electropolishing can take place.

CONCLUSIONS

It is believed that the addition of C.T.A.B. has two beneficial influences on the electropolishing of copper in orthophosphoric acid solutions. First,

the C.T.A.B. is adsorbed on the anode surface and supplements the action of the normal anodic film in improving the micropolishing action of the bath. Second, the C.T.A.B. is adsorbed on the surfaces of oxygen bubbles and accelerates their release from the anode surface, which markedly decreases the size of the pits formed.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

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Mechanisms of Hydrogen Producing Reactions on Palladium[1]

JAMES P. HOARE AND SIGMUND SCHULDINER

Naval Research Laboratory, Washington, D. C.

ABSTRACT

The hydrogen overvoltage on palladium in H_2SO_4 and $H_2SO_4 + Na_2SO_4$ solutions was determined. Data showed that the overvoltage curves could be divided into three consecutive regions: (*A*) η was linearly dependent on i; (*B*) there was a Tafel relationship between η and i in which the b slope, depending on the *p*H of the solution, was equal to 0.030 to 0.042; (*C*) depending on the *p*H of the solution, there was either a Tafel relationship between η and i with a b slope of 0.12, or η was virtually independent of i.

Hydrogen overvoltage mechanisms were postulated for each of these regions.

INTRODUCTION

The study of hydrogen overvoltage on palladium is complicated by the high solubility of hydrogen in this metal. Compared to the platinum cathode, $Pt(H_2)/H^+$, the palladium cathode may be represented by $PdH_x(H_2)/H^+$. The palladium-hydrogen system can exist in two distinct crystallographic phases (1) which are referred to as the α and β phases.

In this investigation the palladium cathode was initially saturated with hydrogen by cathodizing at a high current density. This converted the cathode to a β-palladium-hydrogen system. The hydrogen overvoltage was then measured over a current density range in which this electrode system was maintained.

EXPERIMENTAL METHOD

The experimental method was essentially the same as in reference (2) except that palladium (99.7+ % pure) was substituted for the platinum cathode. For data reported here the temperature was maintained at 39 ± 1° C. In addition, preliminary data were also obtained at 25 ± 1°; this work was not completed, but the results did agree satisfactorily with those of the higher temperature work. The temperature coefficient was too small to determine the activation energy.

The palladium cathode was activated differently from the platinum one. For solutions containing sodium sulfate, the palladium electrode was anodized at 10 ma for 30 min; for the more acid solutions it was anodized at 5 ma for 15 min. In all cases the electrode was then cathodized at 50 ma for at least 30 min before the run was started. At the start of the run the current was lowered to about 5 ma and was kept at this value until a steady-state reading was obtained. The current was then lowered by convenient increments, and overvoltage measurements were taken. After the minimum current was applied the current was increased stepwise to the highest value at which reliable results could be obtained. Measurements for at least three such cycles were recorded. All recorded overvoltage measurements were corrected for solution *IR* drop, and concentration polarization was kept at a minimum by vigorous stirring with a stream of hydrogen.

According to Smith (1), the solid binary alloy, palladium-hydrogen, is produced by the diffusion of hydrogen into the already crystalline metal. The solid phases are a result of the expansion of the face-centered cubic lattice of palladium. The α-phase is formed by an expansion from the lattice-constant value for pure palladium of 3.883 Å to an only slightly higher value of about 3.894 Å. At room temperature, after absorption of some 30 relative volumes of hydrogen, the lattice becomes unstable and some of the crystal grains expand to a new, stable β-phase whose lattice-constant is about 4.02 Å. When the ratio of hydrogen to palladium is equal to about 0.6, all of the palladium is in the β-phase.

In this investigation, the palladium electrode was cathodized at a high current density so that it would be completely converted to the β-phase. During the lowering of current, care was taken not to reach a current density so low that there would be an appreciable reversion to the α-phase.[2] The $\beta \rightarrow \alpha$ transition was evident by a gradual lowering of potential with time. Once the transition current was reached and the α and β phases were simultaneously present, the potential was time dependent and would become more positive as the ratio α/β increased, until a potential 50 mv positive to the

[1] Manuscript received October 25, 1954.

[2] Hanawalt (3) cathodically charged palladium in weak sulfuric acid solution at 0.0001 amp/cm² (20°) and found that the lattice-constant of the resulting palladium-hydrogen alloy was equal to 4.017 Å. This corresponded to the β-phase. The minimum current density used in obtaining overvoltage data was about 0.001 amp/cm².

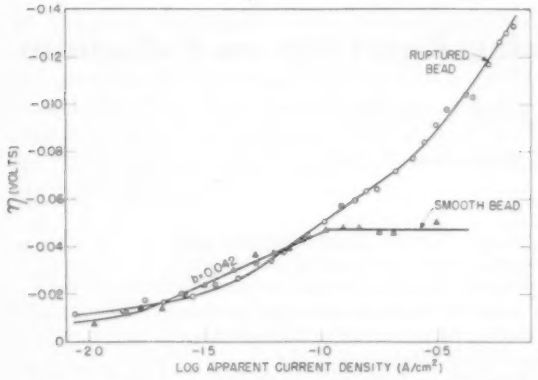

FIG. 1. Anomalous hydrogen overvoltage measurements owing to ruptured palladium cathode (in 2N H_2SO_4).

reversible hydrogen electrode in the same solution was reached. This was shown by Stout[3] (4) who found that when the hydrogen-palladium atomic ratio is less than 0.35, the palladium potential was positive to the reversible hydrogen electrode. This transition was slow, but usually took place overnight. If a clean palladium electrode which had not been cathodized previously was placed in an acid solution which was saturated with hydrogen, its potential was also 50 mv positive to a hydrogen electrode in the same solution. Similar results were obtained by Stout (4), and Hitzler and Knorr (6). It is believed that this potential represents palladium in the α-phase. When such an electrode was polarized at low current densities, the polarization potentials were lower than the potentials for β-palladium.

The palladium electrode was prepared by melting the end of a palladium wire with an oxy-gas flame. The apparent area of the beads ranged from 0.03–0.05 cm². It would have been very difficult to determine the true area of these electrodes, as was done for platinum (7), because of the area changes which took place during polarization. In most cases a newly prepared palladium bead was used for each overvoltage determination. These beads were initially bright and smooth; at the end of a run they were somewhat roughened and grayish in color. For a normal run there was no evidence of cracking or deep pitting of the cathode. However, with extensive cathodic polarization, deep pits, cracks, and blisters were evident. Electrodes which underwent such treatment gave abnormal results. A typical plot of such an electrode, compared with that of a normal run, is shown in Fig. 1. These anomalous results were interpreted as concentration polarization effects which took place in the ruptured areas. For high pH solutions cracking and pitting occurred so slowly that the same bead could be used for several runs, but for low pH solutions the effects were more serious, and a new bead was prepared for each run.

The initial cathodic treatment at 50 ma roughened the surface to such an extent that for the η vs. log i relationship there was an insignificant area change during a single run. The surface cleanliness of the palladium bead was determined both by pseudo-capacitance measurements (7) and by the tests listed in reference (2).

RESULTS

Fig. 2 shows curves for the palladium-hydrogen overvoltage, η, vs. log of apparent current density, i, in the indicated solutions. The points given are average readings for the given current density. The actual maximum spread for each point is ±2.5 mv.

In Fig. 2a are shown curves representing the pH range, 0.84–1.8 (same palladium bead used for all curves). These curves are divided into three regions. The first region, at the lowest current densities, shows a linear relationship between current density and overvoltage. The middle region shows a linear relationship between η and log i with Tafel b slopes progressing from 0.030 at pH 1.8 to 0.042 at pH 0.84. The third region, at the highest current densities, also shows a linear relationship between η and log i, but with a b slope of about 0.12. The more acid solutions shown in Fig. 2b and Fig. 3 also indicate three ranges, the first two sections being essentially the same as for the pH 0.84 curve in Fig. 2a. However, the third section, at the highest current densities, flattens out and in this range η is virtually independent of current density. This corroborates the results of Clamroth and Knorr (8) who, in a study of hydrogen overvoltage on palla-

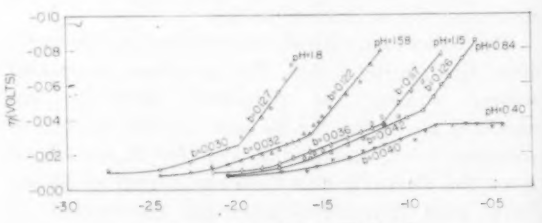

FIG. 2a. Hydrogen overvoltage on palladium. ⊙—0.065N H_2SO_4 + 1N Na_2SO_4, pH 1.8; △—0.202N H_2SO_4 + 1N Na_2SO_4, pH 1.58; ◇—0.376N H_2SO_4 + 0.7N Na_2SO_4, pH 1.15; ⊡—0.514N H_2SO_4 + 0.5N Na_2SO_4, pH 0.84; ▽—1.05N H_2SO_4, pH 0.40.

[3] Several investigators (5) have shown that β-palladium is stable with respect to α-palladium at room temperature and a hydrogen partial pressure of one atmosphere. This work was all done in the absence of solution. In the presence of an aqueous solution of hydrogen ions, as was the case in this investigation, the stability of the beta phase with respect to the alpha phase was evidently altered.

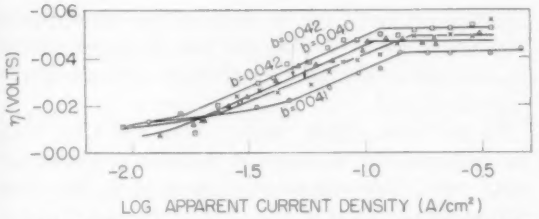

FIG. 2b. Hydrogen overvoltage on palladium. ⊡—3.45N H_2SO_4; △—2.40N H_2SO_4; ×—5.10N H_2SO_4; ⊙—1.05N H_2SO_4.

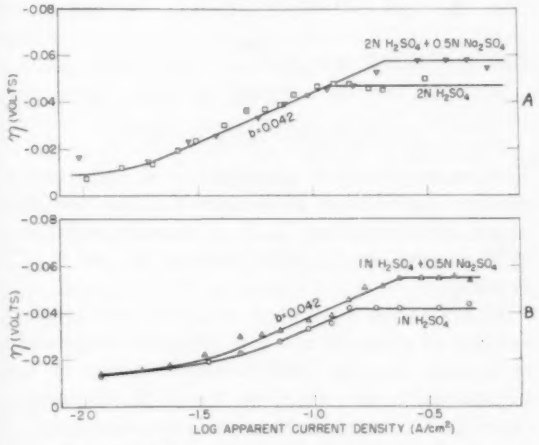

FIG. 3. Salt effect on hydrogen overvoltage

dium in 2N sulfuric acid solution, found that overvoltage was independent of current density after a similar limiting overvoltage was reached. They claimed that this limiting value of overvoltage remained constant to current densities as high as 50 amp/cm².

Fig. 3 shows the effects of adding 0.5N sodium sulfate to 1 and 2N sulfuric acid solutions. For the 1N sulfuric acid solution a weighed amount of sodium sulfate was added to the cell after the overvoltage curve for the pure acid was obtained.

DISCUSSION

By the use of the interrupter technique (7) the current could be cut off in an interval of 5×10^{-8} sec. The potential-time trace observed on the oscilloscope showed a rectangular pulse without rounding off and with a flat top [as in reference (7), Fig. 1a]; however, there was a small ringing effect on the leading edge. This was the result of a small a-c voltage component which was caused by the hydrogen bubble formation at the electrode surface. The rectangular pulse showed that there was initially a very rapid (faster than 5×10^{-8} sec) potential decay which was due to the IR drop from the reference electrode to the double layer at the cathode interface. This interpretation is supported by the existence of a linear (ohmic) relationship between this potential decay and current.

The absence of a measurable polarization decay during an interruption interval of about 1000 μsec showed a pseudocapacitance effect which is normal for such a reversible-electrode system.

These results contradict the contention of Frumkin and Aladjalova (9) and Knorr and coworkers (6, 8) that the overvoltage on palladium can be divided into a rapidly decaying component which they call η_1 and a slowly decaying component, η_2. The initial rapid drop in potential (their η_1) is merely an ohmic IR drop, the slow potential decay (their η_2) is the total hydrogen overvoltage η. In fact, Knorr [reference (10), Fig. 2] found a linear relationship between η_1 and current density; however, he did not interpret this as a purely ohmic drop.

Since the overvoltage curves for palladium can be divided into three regions, each of these are discussed separately.

Region in which $\eta = a - i/k$.—In this zone there is an appreciable reverse reaction taking place. Fig. 4 shows a plot of overvoltage as a function of current density at low current densities. The data are taken from a smooth curve drawn through the points shown in Fig. 2a. The relationship between the rate constant, $k = di/d\eta$, and pH is shown in Fig. 5. This relationship can be expressed as:

$$-(di/d\eta)_{pH\ 0.4-1.8} = 4.07 - 1.96\ p\text{H} \qquad \text{(I)}$$

Similarly, for a platinum cathode (2):

$$-(di/d\eta)_{pH\ 0.5-2.7} = 0.165 - 0.052\ p\text{H} \quad \text{(II)}$$

A comparison of these relationships shows that the rate of change of the rate constant k with pH (dk/dpH) for the reversible hydrogen reaction near equilibrium is greater by a factor of about 38 on β-palladium than on platinum. This is a qualitative

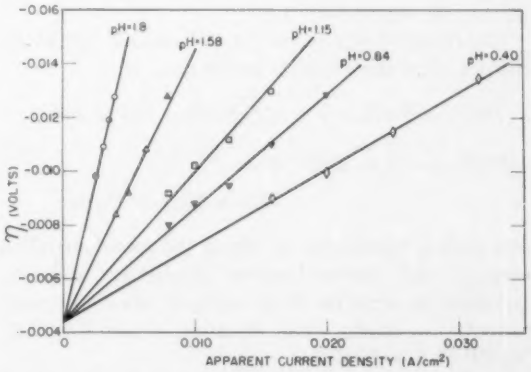

FIG. 4. Hydrogen overvoltage in the range in which η is linearly dependent on current density. (See Fig. 2a for solution composition for given pH values.)

comparison only since the current density on the platinum electrode was corrected for the true area, whereas this was not done for palladium.

The zero intercept, a, shown in Fig. 4 is 0.0044 v. This is presumably the extrapolated open circuit potential of the β-palladium electrode vs. the hydrogen electrode in the same solution. The β-palladium electrode is a reversible hydrogen electrode but is not equivalent to the reversible hydrogen electrode on platinum. It is suggested that this is because the hydrogen solubility in β-palladium gives, in effect, a hydrogen partial pressure slightly higher than atmospheric. Since the minimum ratio of hydrogen to palladium for the β-phase is about 0.6, the β-palladium hydrogen alloy can be represented by $PdH_{0.6}$. This formula does not necessarily represent a hydride formation; however, it has been shown both theoretically and experimentally (1, 4, 11) that one hydrogen solution process ceases at about H/Pd = 0.6. Above this ratio the dissolution of hydrogen becomes more difficult, but a hydrogen-palladium ratio of approximately 1 can be reached.

Region in which $\eta = a - (0.030$ to $0.042) \log i$.—Fig. 2 shows a transition from a Tafel b slope of 0.030 at pH 1.8 to 0.042 in strong sulfuric acid solutions. The 0.030 slope indicated that the reaction mechanism is:

$$H_3O^+ + PdH_{<0.6} + e \rightleftharpoons (PdH_{0.6})-H + H_2O$$
$$(PdH_{0.6})-H \xrightleftharpoons{\text{slow}} \tfrac{1}{2}H_2 + PdH_{0.6} \qquad \text{(III)}$$

Such a mechanism in which the rate-controlling step is the combination of hydrogen atoms gives the Tafel equation:

$$\eta = a - 2.3(RT/\alpha F) \log i \qquad \text{(IV)}$$

where $\alpha = 2$ (the other symbols have their usual meaning). At 39°C, $2.3(RT/2F) = b = 0.0309$. This is the slope which was obtained experimentally in the pH region 1.58–1.8.

The 0.040–0.042 slope for pH values $\leqq 0.84$ indicates that the reaction mechanism is:

$$H_3O^+ + PdH_{<0.6} + e \rightleftharpoons (PdH_{0.6})-H + H_2O$$
$$(PdH_{<0.6})-H + H_3O^+ + e \xrightleftharpoons{\text{slow}} H_2 + H_2O + PdH_{0.6} \qquad \text{(V)}$$

For such a mechanism in which the rate-controlling step is the electrochemical discharge, and the polarization is not far displaced from the equilibrium potential, α in the Tafel equation equals 3/2 (12). At 39° C, $b = 0.0412$.

These results clearly indicate that both mechanisms (III) and (V) are occurring on the palladium cathode at all pH values. However, at high pH values the hydrogen ion concentration in the double layer is relatively low, so most of the current goes into mechanism (III). At low pH the hydrogen ion concentration is high enough that mechanism (V) is predominant.

In the intermediate range (about pH 1.15) both mechanisms can be assumed to occur at about the same rate. This results in a slope such that b is between 0.03 and 0.04.

Region in which $\eta = a - 0.12 \log i$ or η is nearly independent of i.—Fig. 2 shows that from pH 0.84–1.8 the b slope is equal to about 0.12. This indicates that the rate-controlling reaction mechanism is:

$$H_2O + (PdH_{0.6}) + e \xrightleftharpoons{\text{slow}} (PdH_{0.6})-H + OH^- \qquad \text{(VI)}$$
$$(PdH_{0.6})-H \rightleftharpoons \tfrac{1}{2}H_2 + PdH_{0.6}$$

The reason water is assumed to be the primary reactant rather than hydronium ion has been discussed in detail earlier (2, 7). The α for mechanism (VI) is equal to ½ which results in $b = 0.1235$ at 39° C.

At pH values lower than about 0.8 and at overvoltages of about 50 mv, η is virtually independent of current density; this is true whether or not sodium ion is present (Fig. 2 and 3). A possible explanation is that for these higher acid concentrations there is saturation of the β-palladium with atomic hydrogen at the levelling off point. Under these conditions (1), the hydrogen-palladium ratio is approximately 1, and the lattice-constant is at

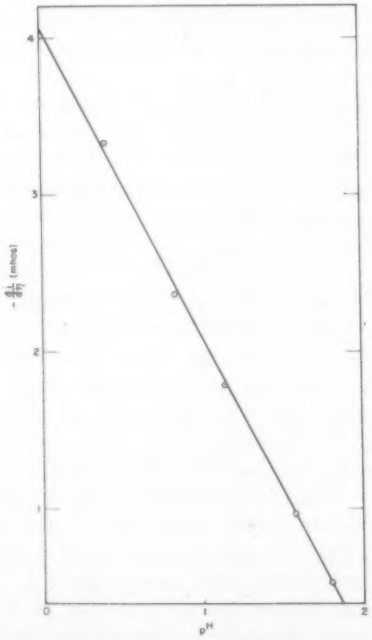

FIG. 5. Effect of pH on the rate of the over-all hydrogen producing reaction in the range in which η is linearly dependent on current density.

its maximum (about 4.06 Å). At current densities above this limiting value, the mechanism for hydrogen production may be represented by:

$$H_3O^+ + e \xrightleftharpoons{(PdH_{0.6}) - H_{sat'd.}} \tfrac{1}{2}H_2 + H_2O \quad \text{(VII)}$$

The cathode material is now completely saturated with atomic hydrogen and is in effect a new electrode system at equilibrium. For such a reversible system near equilibrium there is a linear relationship between η and i:

$$i = (0.050 - \eta)k$$

where k is a rate constant equal to $-di/d\eta$. Since the data show that η is independent of i, the rate constant k must then be so large that the experimental technique used cannot detect changes in overvoltage with i for the current range covered.

The effect of added sodium ion (Fig. 3) was to raise the overvoltage at which the levelling off took place. This results because some of the hydrogen ions in the double layer were replaced by sodium ions which in effect reduced the hydrogen ion activity.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

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High Pressure Oxidation of Metals

Oxidation of Metals Under Conditions of a Linear Temperature Increase[1]

JOHN P. BAUR, DONALD W. BRIDGES, AND W. MARTIN FASSELL, JR.

Department of Metallurgy, University of Utah, Salt Lake City, Utah

ABSTRACT

The oxidation behavior of metals was studied by subjecting the metal sample to a linear temperature increase at constant oxygen pressure. The advantages of this method over previous isothermal methods are that (*a*) a rapid preliminary examination of the oxidation behavior of any metal or alloy over a desired temperature and pressure range can be made quickly, (*b*) the region of pressure dependence usually can be found in a single experiment, (*c*) the number of samples needed is greatly reduced, and (*d*) the method serves as a guide for isothermal measurements at constant pressure.

The linear temperature increase method was applied to Ta, Nb, Mo, Cu, Zr, Mg, Ti, and W. Results are in good agreement with those of previous investigations made in this laboratory.

Theoretical considerations show that the results could be explained by imposing the conditions of a linear temperature increase on a general type rate equation.

INTRODUCTION

Prior to this time, the oxidation behavior of metals at high pressures has been determined by measuring oxidation rates at a series of constant temperatures and oxygen pressures. This method, although entirely satisfactory, is time consuming in that a separate sample must be used for each determination. This is particularly true in the preliminary search to ascertain the region wherein the pressure effect is most pronounced for a metal whose oxidation characteristics at high pressures are completely unknown. It would be desirable, therefore, to have a method whereby oxidation behavior could be surveyed quickly and the pressure sensitive region found. Such a method has been developed here.

The method consists of measuring the gain in weight of a metal at constant oxygen pressure while, at the same time, the metal temperature is increased in a linear manner. Similar methods have had wide application in the field of differential thermal analysis, and Olmer (1) has recently applied this technique to the reduction of iron oxides by hydrogen at atmospheric pressure.

EXPERIMENTAL TECHNIQUE

A linear temperature increase of approximately 5°C/min was obtained in one of the standard high-pressure furnaces (2) by modifying a standard Leeds & Northrup Micromax Controller. This was accomplished by connecting a small synchronous motor-driven worm and worm gear drive unit to the controller set point. The controller then follows this linear increase in the set point, thereby raising the temperature of the furnace at a linear rate. The temperature of the guard windings must be manually increased to keep pace with the center winding. The rate of temperature increase varies slightly over the range of temperature covered, i.e., 400°–1000°C, because of the large thermal inertia of the furnace used and the absence of automatic controls on the guard ring windings. This thermal inertia also prevents the furnace from cooling quickly, requiring several hours to cool to starting temperature.

The operating procedure is as follows. The sample is introduced in the usual fashion (2, 3), and the furnace flushed several times with oxygen and pressurized to the desired oxygen pressure. A starting temperature is selected and the furnace allowed to reach equilibrium at this temperature. Simultaneously the sample is raised into the hot zone and the motor drive on the recorder is energized. The sample is allowed to remain in the hot zone a sufficient time to form a film 10^{-2} to 10^{-3} cm thick (calculated from mass gain data). This thickness is necessary in order to rule out such considerations as logarithmic and cubic oxidation laws and other electrostatic and nonequilibrium effects. At regular time intervals, the temperature is read on a Leeds & Northrup type (8662) potentiometer, and the gain in weight of the sample is determined by measuring the elongation of a helical quartz spring on which the sample is suspended. Data are recorded in the form of curves showing weight gained per unit of surface area as a function of temperature.

[1] Manuscript received November 1, 1954. This paper was prepared for delivery before the Cincinnati Meeting, May 1 to 5, 1955.

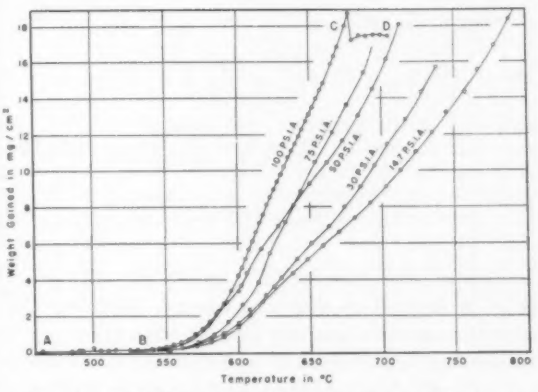

FIG. 1. Oxidation of tantalum under conditions of a linear temperature increase of 5°C/min.

INVESTIGATION OF THE OXIDATION OF TANTALUM IN OXYGEN WITH LINEAR TEMPERATURE INCREASE

In order to test the method it was decided to investigate the behavior of tantalum in oxygen because this metal had been thoroughly investigated previously (3) and all energy values were known. Fig. 1 shows the plot of weight gained per unit surface area as a function of temperature for five oxygen pressures: 14.7, 30, 50, 75, and 100 psia. From these curves, three temperature regions are apparent: A–B, a lower horizontal region, in which the oxidation rate is either too low to be recorded by the weighing system or is insensitive to pressure; B–C, a curved "knee" portion over which the metal is pressure sensitive, i.e., the slope of the curve (a function of the oxidation rate, dm/dt) changes with temperature and pressure; and C–D, upper horizontal portion indicating that the metal has been completely oxidized.

It has been found that the region B–C is in agreement with oxidation rate curves for tantalum at various pressures [Fig. 6 of reference (3) which shows an increase in rate in the region 550°–650°C and a decrease in the region 650°–750°C].

THEORETICAL CONSIDERATIONS

Work in this laboratory has shown a general type of rate equation for pressure sensitive oxidation of the form:

$$\frac{dm}{dt} = k_o f(\theta)\,\frac{kT}{h}\exp\left[\frac{-\Delta F^{\ddagger}}{RT}\right] = k_o f(\theta)\,\frac{kT}{h}\exp\left[\frac{-\Delta H^{\ddagger}}{RT}\right]\exp\left[\frac{\Delta S^{\ddagger}}{R}\right] \quad \text{(I)}$$

$$m\,\frac{dm}{dt} = C_o f(\theta)\,\frac{kT}{h}\exp\left[\frac{-\Delta F^{\ddagger}}{RT}\right] = C_o f(\theta)\,\frac{kT}{h}\exp\left[\frac{-\Delta H^{\ddagger}}{RT}\right]\exp\left[\frac{\Delta S^{\ddagger}}{R}\right] \quad \text{(II)}$$

where m is the mass increase per unit of surface area; k_o is a proportionality constant with the dimensions of ML^{-2} and includes the correction factor for the true surface area (surface roughness and number of active sites per surface area) involved in the oxidation reaction; C_o is a constant for the parabolic case discussed in detail in Appendix II; and θ is the fraction of surface sites covered. The other terms retain their customary significance as in the Eyring theory (4, 5) with the transmission coefficient equal to unity. Equation (I) is applicable to linear oxidation, while equation (II) is the corresponding expression for parabolic oxidation, in a region where the oxidation rate is pressure sensitive (i.e., in a region where the oxidation rate is a function of the external concentration of oxygen).[2]

Experimental restrictions of an imposed linear temperature increase result in a possible variable substitution:

$$T = b\cdot t + c \quad \text{(III)}$$

or

$$dT = b\cdot dt \quad \text{(IV)}$$

where T is the absolute temperature; t is the time; b is the rate of increase of temperature per unit time; and c, the starting temperature in degrees Kelvin.

Incorporation of equation (IV) in equation (I) results in an expression for the mass increase per unit of surface area, under the conditions of linear temperature increase as given in equation (V)

$$\Delta m = \int_o^m dm = \frac{k_o' k}{bh}\int_{T_o}^{T} f(\theta)\,T\exp\left[-\frac{\Delta H^{\ddagger}}{RT}\right]dT \quad \text{(V)}$$

where $k_o' = k_o\cdot e^{\Delta S^{\ddagger}/R}$ because the term $e^{\Delta S^{\ddagger}/R}$ is here assumed to be temperature independent over the range of temperatures used. Knowledge of the concentration term, $f(\theta)$, as a function of temperature would allow evaluation of the integral—by graphical means if no other method of solution were feasible.

Judicious choice of experimental conditions results in two limiting cases of equations (I) and (II) which are resolvable into standard functions and a tabled definite integral, the exponential integral. The concentration term, $f(\theta)$, is here assumed, as in reference (3), to be

$$f(\theta) = \theta = \frac{K_1\cdot[O_2]}{1 + K_1\cdot[O_2]} \quad \text{(VI)}$$

where K_1, the equilibrium constant for the adsorption process, is represented as a function of temperature by

$$K_1 = e^{-(\Delta F/RT)} = e^{-(\Delta H/RT)}\cdot e^{\Delta S/R} \quad \text{(VII)}$$

[2] *See* Appendix II for a discussion of this point.

and the effective surface concentration of the oxygen in terms of the external gas concentration $[O_2]$ is given by:

$$[O_2] = \frac{n}{V} = \frac{P}{RT} \qquad \text{(VIII)}$$

This is in accordance with reference (3) on tantalum. The function, $f(\theta)$, could possibly be much more complex.

Substituting equation (VI) into equation (V) one obtains:

$$\Delta m = \frac{k_o' k}{bh} \int_{T_o}^{T} \theta T \exp\left[-\frac{\Delta H^\ddagger}{RT}\right] \cdot dT = \frac{k_o' k}{bh} \int_{T_o}^{T} T \exp\left[-\frac{\Delta H^\ddagger}{RT}\right] \cdot \frac{K_1[O_2]}{1 + K_1[O_2]}\, dT \qquad \text{(IX)}$$

Substitution of equations (VII) and (VIII) into equation (IX) yields the following expression for the mass increase:

$$\Delta m = \frac{k_o' k}{bh} \int_{T_o}^{T} T \cdot \exp\left[-\frac{\Delta H^\ddagger}{RT}\right] \cdot \left\{\frac{P/RT \cdot \exp(\Delta S/R) \exp(-\Delta H/RT)}{1 + P/RT \cdot \exp(\Delta S/R) \exp(-\Delta H/RT)}\right\} dT \qquad \text{(X)}$$

If $\theta \ll 1$, $P/RT \cdot e^{\Delta S/R} \cdot e^{-\Delta H/RT}$ can be neglected in the denominator of equation (IX) resulting in the first approximate solution of equation (X), i.e., the limiting case for small surface coverage:

$$\Delta m = -\frac{P}{R} \exp\left[\frac{\Delta S}{R}\right] \frac{k_o' k}{bh} \cdot \int \frac{1}{x^2} \exp\left[\frac{-(\Delta H^\ddagger + \Delta H)}{R}\, x\right] dx \qquad \text{(XI)}$$

where $x = 1/T$ and $dT = -dx/x^2$.

Integration[3] of equation (XI) yields:

$$\Delta m = \frac{k_o' k}{bh} \frac{P}{R} \exp\left[\frac{\Delta S}{R}\right] \left\{T \exp\left[-\frac{(\Delta H^\ddagger + \Delta H)}{RT}\right] - \left[\frac{(\Delta H^\ddagger + \Delta H)}{R}\right] \cdot \left[-Ei\left(-\frac{(\Delta H^\ddagger + \Delta H)}{RT}\right)\right]\right\} \qquad \text{(XII)}$$

where

$$-Ei(-x) = \int_x^\infty \frac{e^{-u}}{u} \cdot du; \quad x > 0$$

is called the exponential integral. This function is tabled (6, 7).

For the limiting case of complete surface coverage, i.e., $\theta = 1$, a pressure independent equation results from equation (IX) by a change in variable as in equation (XI).

$$\Delta m = -\frac{k_o' k}{bh} \int \frac{1}{x^2} \exp\left[-\frac{\Delta H^\ddagger}{R}\, x\right] dx \qquad \text{(XIII)}$$

[3] Integral 302, p. 262, "Handbook of Chemistry and Physics," 31st ed., Chemical Rubber Publishing Co., Cleveland (1949).

Integration yields

$$\Delta m = \frac{k_o' k}{bh} \left\{\tfrac{1}{2}\left[-T^2 \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) + \frac{\Delta H^\ddagger}{R}\, T \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) + \left(\frac{\Delta H^\ddagger}{R}\right)^2 \left\{-Ei\left(-\frac{\Delta H^\ddagger}{RT}\right)\right\}\right]\right\} \qquad \text{(XIV)}$$

Equations (XII) and (XIV) point the way to a possible method of obtaining energy values for the heat of activation and the heat of adsorption.

Graphical integration of equation (X) was chosen to fit the data for tantalum over the entire temperature range at any one pressure because either of the limiting case equations (XI) and (XIII) fails when applied to the entire range of surface coverage, i.e., $0 \leqq \theta \leqq 1$.[4]

In the case of tantalum, the data of Peterson and coworkers (3) provides a test for equation (V) and further substantiates the postulated mechanism of oxidation of tantalum. For tantalum, equation (X) is applicable. The following values of involved energies are available: $\Delta H = -27{,}350$ cal/mole; $\Delta H^\ddagger = 29{,}500$ cal/mole (600°–800°C); $\Delta S = 22.58$ entropy units. Equation (X) becomes for graphical integration:

$$\Delta m = \left\{1.509 \times 10^{-6}\, \frac{k_o' k}{bh}\right\} \int_{873}^{T} \frac{T \cdot \exp(-1075/T)}{T/P + 1.509 \times 10^{-6} \exp(13{,}675/T)}\, dT \qquad \text{(XV)}$$

where P is in atmospheres.

The test of the method can then be made by applying equation (XV) to the data on tantalum and using graphical integration to evaluate the integral. Equation (XV) can be rewritten as:

$$\{\Delta m_T - \Delta m_{T_o}\} \left\{\int_{873}^{T} \frac{T \cdot \exp(-1075/T)}{T/P + 1.509 \times 10^{-6} \exp(13{,}675/T)}\, dT\right\}^{-1} = \text{const.} \qquad \text{(XVI)}$$

or

$$\frac{\Delta m_T - \Delta m_{T_o}}{\Sigma} = \text{constant} = C \qquad \text{(XVII)}$$

where Σ is the value of the definite integral. Table I shows the application of equation (XVI) to the data used to obtain Fig. 1. The agreement of the constants of Table I for each pressure is striking, but it will be noted that those for the pressures 14.7 and 100 psia are not in as good agreement with the other pressures as might be desired. These anomalies can be explained by considering the fol-

[4] *See* Appendix I for a discussion of this point.

TABLE I. *Application of equation (XVI) to the data of tantalum oxidized under conditions of a linear increase in temperature*

14.7 psi				30 psi				50 psi				75 psi				100 psi			
°C	Σ	$\frac{\Delta m}{-\Delta m_{T_o}}$	C	°C	Σ	$\frac{\Delta m_T}{-\Delta m_{T_o}}$	C	°C	Σ	$\frac{\Delta m_T}{-\Delta m_{T_o}}$	C	°C	Σ	$\frac{\Delta m_T}{-\Delta m_{T_o}}$	C	°C	Σ	$\frac{\Delta m_T}{-\Delta m_{T_o}}$	C
608	2.327	0.657	0.282	608	4.694	0.741	0.159	606	7.688	1.303	0.170	614	15.809	1.263	0.080	610	18.712	1.991	0.106
617	4.971	1.396	0.281	619	11.232	1.540	0.137	616	17.448	2.649	0.152	622	27.528	2.842	0.103	619	35.919	3.810	0.106
625	7.345	2.238	0.305	630	17.886	2.514	0.141	628	29.393	3.912	0.133	633	43.935	4.541	0.103	630	57.409	5.517	0.096
638	11.272	2.990	0.265	641	24.662	3.545	0.144	639	40.550	5.072	0.125	644	60.659	6.248	0.103	641	79.414	7.131	0.090
648	14.352	3.753	0.262	651	30.919	4.424	0.143	650	51.932	6.242	0.120	654	76.177	7.849	0.103	651	109.798	8.838	0.080
659	17.790	4.499	0.253	663	38.568	5.344	0.139	662	64.609	7.392	0.114	666	95.158	9.477	0.100	661	130.625	10.740	0.082
670	21.286	5.248	0.247	674	45.722	6.415	0.140	673	76.436	8.622	0.113	676	111.245	10.993	0.099	670	149.683	12.840	0.086
681	24.830	6.023	0.243	685	52.965	7.522	0.142	684	88.439	10.001	0.113	688	130.870	12.794	0.098				
692	28.419	6.842	0.241	695	59.614	8.682	0.143	694	99.504	11.457	0.115	696	144.151	14.831	0.103				
703	32.045	7.727	0.241	704	65.671	9.870	0.150	704	110.702	13.132	0.119								
713	35.379	8.635	0.236	711	74.541	11.222	0.151	713	120.879	15.034	0.124								
724	39.102	9.683	0.248	728	82.128	12.713	0.155												
735	42.848	10.731	0.250	738	89.108	14.133	0.159												

lowing. In the case of 14.7 psia it can be seen by examination of equation (XVI) that this equation is extremely sensitive in the region about $P = 1$ atm or 14.7 psia. A slight increase in the absolute pressure yields a value for the constant more consistent with those obtained at the other pressures. For example, if the pressure were actually 16 psia (which is entirely possible because of the difficulty of setting the oxygen at 1 atm using the high pressure gauges, and the pressure increase due to the increase in temperature from 400° to 800°C), the value of the constant would be changed by 8%. In the case of the 100 psia run, the difference can possibly be explained by considering the high oxidation rate and the difficulty of following this rapid weight increase with the cathetometer telescope. Equation (XVI) is far less sensitive at 100 psia than at 14.7 psia. A slight increase in the value of $\Delta m_T - \Delta m_{T_o}$ would result in a more consistent value of the constant.

Investigation of the Oxidation of Copper

Previous work in this laboratory on copper (8) has shown the oxidation rate to be independent of oxygen pressure between 1 atm and 20.4 atm. Evaluation of more recent data results in an energy of activation of 31,605 cal/mole (100–300 psia) and 31,437 cal/mole (1 atm) for the temperature range 700°–1000°C (9). Using equation (VI) of Appendix II, the general type of rate equation for parabolic oxidation can be integrated to yield an expression similar to equation (XIV) as follows:

$$\Delta m^2 = \frac{C_o' k}{bh}\left\{\frac{\Delta H^\ddagger}{R}T\exp\left[-\frac{\Delta H^\ddagger}{RT}\right] + \left(\frac{\Delta H^\ddagger}{R}\right)^2 \left\{-Ei\left(-\frac{\Delta H^\ddagger}{RT}\right)\right\} - T^2\exp\left[-\frac{\Delta H^\ddagger}{RT}\right]\right\} \quad \text{(XVIII)}$$

where: $C_o' = C_o e^{\Delta s^\ddagger/R}$.

TABLE II. *Application of equation (XVIII) to data of high purity OFHC copper oxidized under conditions of a linear increase of temperature*

14.7 psia				100 psia			
°C	$\frac{\Delta m_T^2 - \Delta m_{T_o}^2}{}$	$\Sigma_T - \Sigma_{T_o}$	C	°C	$\frac{\Delta m_T^2 - \Delta m_{T_o}^2}{}$	$\Sigma_T - \Sigma_{T_o}$	C
715	0.473	0.620	0.763	714	0.273	0.475	0.575
726	0.909	1.368	0.664	726	0.879	1.198	0.733
738	1.508	2.277	0.662	737	1.341	1.981	0.677
750	2.404	3.374	0.713	748	2.156	2.918	0.739
762	3.290	4.466	0.736	759	2.891	4.041	0.715
773	4.297	6.120	0.702	771	3.839	5.389	0.713
783	5.374	7.579	0.709	780	4.743	6.596	0.719
796	6.827	9.928	0.688	791	6.080	8.330	0.730
805	8.391	11.679	0.718	802	6.887	10.249	0.672
817	10.143	14.392	0.705	812	8.750	12.336	0.709
829	11.974	17.622	0.680	823	10.545	14.768	0.714
839	14.641	20.430	0.717	834	12.801	17.589	0.728
852	17.766	25.080	0.708	844	15.370	20.611	0.746
862	21.245	28.898	0.735	854	18.227	24.083	0.757
872	25.158	33.239	0.757	865	21.871	28.083	0.779
883	29.727	38.624	0.770	875	26.662	32.298	0.826
895	35.432	45.484	0.779	887	30.824	38.379	0.749

For the temperature range 700°–1000°C the test of equation (XVII) can be made by illustrating that:

$$\frac{\Delta m_T^2 - \Delta m_{700°C}^2}{\Sigma_T - \Sigma_{700°C}} = \text{constant} = C \quad \text{(XIX)}$$

where $\Sigma_T - \Sigma_{T_o}$ is the value of the definite integral between $T = T$ and $T = 700$°C. Table II shows the results of this evaluation applied to the data on high purity OFHC copper subjected to oxidation under a linear temperature increase of 5°C/min.

Agreement between the values of the constants of Table II is excellent and shows that the oxidation behavior of copper can be explained by application of equation (II).

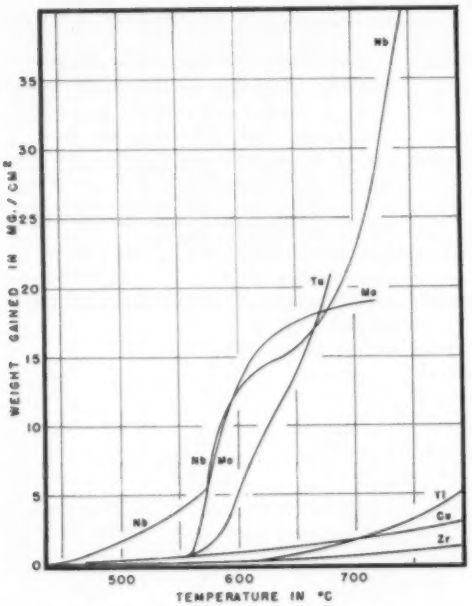

FIG. 2. Oxidation curves for various metals under conditions of a linear temperature increase of 5°C/min and constant oxygen pressure of 100 psia.

OTHER METALS INVESTIGATED

As a preliminary survey, the oxidation behavior of a number of other metals, Nb, Zr, Ti, W, Mg, Mo, in addition to Ta and Cu, were also investigated under conditions of a linear temperature increase. Fig. 2 shows the oxidation curves for Nb, Zr, Mo, Cu, Ta, and Ti over the temperature range 450°–790°C and oxygen pressure of 100 psia. Tungsten was not included on this graph because the pressure sensitive region occurs above 750°C, and the oxidation rates below this temperature are too low to be recorded. The curves clearly show the difference in oxidation behavior between those metals which oxidize according to the linear law (Ta, Nb, and Mo) and those (Cu, Ti, and Zr) which oxidize according to the parabolic law, i.e., in which a protective oxide film is formed.

The oxidation behavior of high purity magnesium is worthy of special mention at this point. Over the temperature range 417°–584°C, the sample gained very little weight (0.064 mg/cm²) until ignition occurred at 591°C.

An interesting comparison can be made between the oxidation behavior of molybdenum and that of tantalum and niobium. The curve of molybdenum shows a pressure sensitive region from 550°–650°C after which the weight gained approaches a limiting value over the temperature range 650°–700°C, as though the metal were forming a protective film. Samples ignited at 725°C. These findings are in excellent agreement with earlier work (10) which

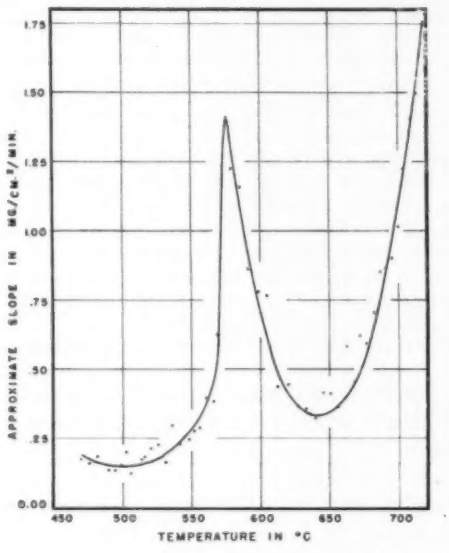

FIG. 3. Curve showing approximate oxidation rate for niobium calculated from the curve of Fig. 2.

gave the following regions for molybdenum: (*A*) no pressure dependence of oxidation rate was found from 500° to 525°C; (*B*) from 550° to 700°C the oxidation rate was sensitive to pressure; and (*C*) a peculiar pressure sensitive transition region 650°–700°C was observed. The curve for tantalum, included here for comparison, was described above.

Niobium oxidizes in a manner similar to that of tantalum but with a more pronounced pressure effect over the temperature region 530°–700°C. The pressure sensitive region is strikingly shown in Fig. 3 in which the slope, determined from the niobium curve of Fig. 2, is plotted against the temperature. This cusped shaped curve is characteristic of metals which oxidize according to equation (I) and is in good agreement with the findings of this laboratory in the investigation of the oxidation of niobium recently completed (11). In regard to Fig. 3, it should be noted that the values of the rate constant are, at best, approximations within the limits of experimental techniques, and should not be used as absolute rate values.

CONCLUSIONS

A method of studying the oxidation behavior of metals in oxygen has been developed in which a metal sample is subjected to a linear increase in temperature at a constant oxygen pressure. The method was found to have the following advantages.

1. It yields a rapid cursory examination of the oxidation behavior of a metal over any desired temperature range.

2. It determines the temperature range over which the oxidation rate is pressure dependent.

3. It consumes a minimum number of samples, using one sample per run.

4. It gives approximate values of the rate constant over the temperature range, and can be used to evaluate values of the activation energy of the reaction and the enthalpy and entropy of adsorption by the solution of equations (XII) and (XIV).[5]

The method was applied to Ta, Nb, Mo, Cu, Zr, Mg, Ti, and W, and experimental results obtained are in good agreement with results of previous investigations of these metals made in this laboratory. It was shown by theoretical considerations that experimental results obtained on tantalum and copper could be explained by imposing the conditions of a linear temperature gradient on a general type of rate equation (developed in this laboratory) for pressure sensitive metals. It is believed that this method shows much promise and will prove to be of considerable value in future investigations of the oxidation behavior of metals and alloys, particularly those about which little or nothing is known.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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[5] Similar conclusions have been reached by H. Eyring and coworkers (12).

APPENDIX I

The range of convergence of the limiting case solutions of equation (X) can best be illustrated by rewriting equation (IX):

$$\Delta m = \int dm = \frac{k_0' k}{bh} \int T \exp\left[-\frac{\Delta H^\ddagger}{RT}\right] \frac{K_1 \cdot [O_2]}{1 + K_1 \cdot [O_2]} \cdot dT \quad \text{(IX}a\text{)}$$

Case I.—$K_1 \cdot [O_2] < 1$, i.e., $\theta < \frac{1}{2}$, using the variable substitution as above, equation (IXa) can be rewritten as follows:

$$\Delta m = -\frac{k_0' k}{bh} \int \left\{ \frac{P}{Rx^2} \exp\left[-\frac{(\Delta H^\ddagger + \Delta H)}{R} x\right] \exp\left[\frac{\Delta S}{R}\right] \right\} \cdot \sum_0^\infty (-1)^n \{K_1[O_2]\}^n \, dx \quad \text{(IX}b\text{)}$$

Upon expansion of the infinite series one obtains:

$$\Delta m = -\frac{k_0' k}{bh} \int \frac{P}{Rx^2} \exp\left[-\frac{(\Delta H^\ddagger + \Delta H)}{R} x\right] \exp\left[\frac{\Delta S}{R}\right] \{1 - K_1[O_2] + K_1^2[O_2]^2 - \cdots\} \, dx \quad \text{(IX}c\text{)}$$

It is obvious that this series converges for all values of $|K_1[O_2]| < 1$ corresponding to $\theta < \frac{1}{2}$. It will also be noted that equation (XI) can be obtained from equation (IXc) by retaining only the first term.

Case II.—$K_1[O_2] > 1$, i.e., $\theta > \frac{1}{2}$.

By multiplying numerator and denominator of equation (IXa) by $1/K_1[O_2]$ one obtains:

$$\Delta m = \int dm = -\frac{k_0' k}{bh} \int T \exp\left[-\frac{\Delta H^\ddagger}{RT}\right] \frac{1}{1 + K_1^{-1}[O_2]^{-1}} \, dT \quad \text{(IX}d\text{)}$$

which, when expanded as in equation (IXb), yields

$$\Delta m = \int dm = -\frac{k_0' k}{bh} \int \frac{1}{x^2} \exp\left[-\frac{\Delta H^\ddagger}{R} x\right] \sum_0^\infty (-1)^n K_1^{-n}[O_2]^{-n} \, dx \quad \text{(IX}e\text{)}$$

Upon expansion as in equation (IXc) one obtains:

$$\Delta m = \int dm = -\frac{k_0' k}{bh} \int \frac{1}{x^2} \exp\left[-\frac{\Delta H^\ddagger}{R} x\right] \left\{1 - \frac{1}{K_1[O_2]} + \frac{1}{K_1^2[O_2]^2} - \cdots\right\} dx \quad \text{(IX}f\text{)}$$

This series converges for all values of $|K_1 \cdot [O_2]| > 1$ corresponding to $\theta > \frac{1}{2}$ and equation (XIII) can be obtained by retaining only the first term of equation (IXf).

APPENDIX II

Clarification of the term pressure sensitive parabolic oxidation seems in order. Pressure sensitivity means that the oxidation rate is effected by the external concentration of the oxygen or, perhaps more realistically, by the concentration of the oxygen chemisorbed on the reaction surface. The effect of surface coverage upon the linear rate of oxidation has been noted above (see page 491 of text), and pressure effects have been observed in the case of parabolic oxidation (1). It should be kept in mind that pressure is not the desired variable but the concentration of the surface oxygen phase. The pressure of the gas is only directly proportional to the concentration of the gaseous phase for constant temperature. For variable temperature

(or in the comparison of one isothermal set of rates with another), the more complete expression, $[O_2] = n/V = P/RT$, should be used. This expression assumes the ideal gas law to hold and that the surface activity of oxygen is directly proportional to the bulk gas phase activity.

As first derived by Tammann (2), the rate of growth of an oxide layer is controlled by the concentration gradient of diffusing atoms; the thickness X of the oxide layer varies with time, t, as:

$$dX/dt = A/X \qquad \text{(Ia)}$$

or,

$$X^2 = 2At + \text{constant} \qquad \text{(Ib)}$$

Mott and Gurney (3) derive the expression for the constant A for a semiconductor to be:

$$A = \Omega D[n_1 - n_2] \qquad \text{(II)}$$

where Ω is the volume of oxide per metal ion, D is the diffusion coefficient, and the bracketed quantity is the concentration gradient of the interstitial migrating cations for excess metal oxides or, for a metal deficit oxide, the concentration of lattice vacancies. This quantity permits three types of concentration gradients, with n_2 and n_1 equal to: (*a*) concentrations of electrons at the respective interfaces when the conductivity of the electron is small compared to that of the ion species; (*b*) twice the concentrations of the metal ions at the respective interfaces when the oxide is a metal excess type semiconductor; and (*c*) twice the concentrations of the oxygen atoms at the respective interfaces when the oxide is a metal deficit type semiconductor, the mobility of metal ions through lattice vacancies in this case is directly proportional to the concentration of the oxygen.

For systems involving an oxygen/oxide interface of type (*a*) or (*b*), pressure sensitivity would not be expected excluding low pressure "oxygen starvation" effects or film growth involving electrostatic potential barriers. Type (*c*) oxide layers in contact with external oxygen would exhibit pressure sensitivity according to the degree of relative surface coverage.

For oxygen excess oxides Mott and Gurney state the following: "Now it was shown that cuprous oxide is a conductor only if it contains an excess of oxygen, and that its conductivity increases with increasing pressure of oxygen in contact with the crystal. On the other hand cuprous oxide in contact with copper is practically of stoichiometric composition. Thus in tarnishing reactions $n_1 \ll n_2$ and the rate of reaction is determined by n_2, the concentration of excess oxygen at the free surface. . . ." (p. 257, *op. cit.*) Hence equation (II) becomes for an oxygen excess semiconductor oxide

$$A \approx -2\Omega Dn_2 = -2\Omega f(\theta) \cdot D \qquad \text{(III)}$$

where $f(\theta) = n_2$, and θ is the fraction of surface covered with chemisorbed oxygen.

According to Eyring (4) the diffusion coefficient, D, should be:

$$D = \lambda^2 \mathrm{K} kT/h \cdot \exp[-\Delta F^{\ddagger}/RT] \qquad \text{(IV)}$$

where λ is the jump distance between interstitial positions in the lattice for metal excess oxides or the corresponding vacancy jump distance for metal deficit oxides; K is the transmission coefficient (usually assumed unity); k is the Boltzmann constant; h is Planck's constant; $\Delta F^{\ddagger}$ is the activation free energy associated with the jump of cations; T is the absolute temperature; and R is the molar gas constant.

Thus equation (II) of text results:

$$m \cdot dm/dt = k_o \cdot A = -2\Omega k_o \cdot f(\theta) \cdot D = C_o \cdot f(\theta) \cdot kT/h \cdot \exp[-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R] \qquad \text{(V)}$$

where $C_o = 2\lambda^2 \cdot (-\Omega) \cdot k_o$, and k_o is defined on page 491 of the text.

The validity of the factor kT/h in the Eyring derivation has been challenged by Zener and others (5, 6). They replace the factor with a frequency of vibration function. However, this is of more theoretical importance than of immediate consequence, as the effect of a linear temperature factor when multiplied by an exponential term containing the variable is but slight.

It should be noted that the above derivation is essentially as that set forth by Gulbransen (7). However, Gulbransen does not distinguish the rate-determining ionic gradient species for the two known types of semiconductors, i.e., metal deficit and metal excess.

Equation (V) does not hold for metal excess semiconductors such as ZnO or Fe_2O_3 where n_2 would be the concentration of metal ions at the free surface. This concentration would be expected to be nearly constant, although recent work (8–10) shows pressure effects for this case.

Where the surface coverage is unity in the case of rate-controlling diffusion through an oxygen excess semiconductor [$f(\theta) = 1$] or where the semiconductor is a metal ion excess oxide [with no dependence on $f(\theta)$], the equation for parabolic growth reduced to

$$m \cdot dm/dt = C_o \cdot kT/h \cdot \exp[-\Delta F^{\ddagger}/RT] \qquad \text{(VI)}$$

The entire temperature dependence now rests with the temperature variation of the diffusion coefficient.

Application of the foregoing arguments is attempted in the text proper for the metal copper in region where two oxides are known to exist in equilibrium with the metal. The semiconductor properties of Cu_2O have been well established (1) but those of the other oxide of copper, CuO, are not well known (9, 11). Thus as the oxygen/oxide interface is probably O_2/CuO in the temperature-pressure range investigated it is impossible to state whether the observed pressure insensitivity of the system is due to complete surface coverage or to the fact that CuO is a type (*a*) or (*b*) semiconductor.

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